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THE ANALYST

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THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

NEW MEMBERS

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Desmond Arthur Sidney Barnes, B.Sc. (Lond.); Thomas Malcolm Blackwood, B.Sc. (Edin.); Bernard Fitzgerald; John Kenneth Fleming, A.R.I.C.; Neil Robert Francis, B.Sc. (Nottingham); Harry William Houghton, B.Sc. (Nottingham); Archie Ronald Javes, B.Sc. (Lond.), F.R.I.C., F.Inst.Pet.; Charles Edward Roland Jones; Derek Edward Kings, B.Sc. (Hull), A.R.I.C.; Frederick Lishman, B.Sc. (Sheff.); Denis Naylor, B.Sc. (Sheff.); John Jonas Nicholls, B.Sc. (Lond.), F.R.I.C.; Stanley Hope Philpot, A.R.I.C.; William Crossley Purdy, B.A. (Amherst), Ph.D. (M.I.T.); Herbert Taylor, B.Sc. (Lond.), A.R.I.C.; Walter Westwood, B.Sc. (Liv.), A.I.M.

Junior Members

Elizabeth Jane Hall, B.Sc. (Wales); David Henry Thow, B.Sc. (Edin.).

DEATH

We record with regret the death of

Daniel Carswell Macpherson.

NORTH OF ENGLAND SECTION and MICROCHEMISTRY GROUP

A Joint Meeting of the North of England Section and the Microchemistry Group with the North Lancashire Section of the Royal Institute of Chemistry was held at 7.30 p.m. on Friday, May 16th, 1958, at Redmans Park House Hotel, North Promenade, Blackpool. The Chair was taken by the Chairman of the North Lancashire Section, Mr. C. D. Lafferty, B.Sc., F.R.I.C.

The following papers were presented and discussed: "The Micro Vacuum Fusion Determination of Gases in Metals," by M. R. Everett; "The Chemical Determination of Nitrogen in Reactor Metals," by J. A. Ryan, A.R.I.C.; "The Determination of Naturally Occurring Radioactive Impurities in a Uranium Purification Process," by M. R. Hayes, A.R.I.C.; "A Simple Manometric Method for the Determination of Carbon in Metals," by M. R. Everett (see summaries below).

The meeting was preceded at 2 p.m. by a visit to the Chemical Services Department Laboratories of the Springfields Works of the United Kingdom Atomic Energy Authority (Industrial Group).

The Micro Vacuum Fusion Determination of Gases in Metals

Mr. M. R. Everett said that, in the vacuum fusion technique, a sample was added to a de-gassed graphite crucible or a de-gassed carbon-containing metal bath, maintained at a high temperature *in vacuo*. The hydrogen, oxygen and nitrogen contents of suitable metals could be calculated from analysis of the evolved gas, which consisted of a mixture of hydrogen, carbon monoxide and nitrogen. Sources of error in vacuum fusion were briefly considered.

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A micro-scale all-mercury-and-glass apparatus was described. This contained a 3·5-g molten-platinum bath at an operating temperature of 1900° C for the analysis of metals such as thorium, zirconium, uranium, niobium, vanadium, molybdenum and tungsten. Sample weights were of the order of 50 mg, and up to twelve samples could be analysed consecutively. A low-pressure circulating-type gas analytical system was used. Limits of detection were approximately 1 p.p.m. for both hydrogen and nitrogen and 5 p.p.m. for oxygen.

The author quoted results that demonstrated the agreement between vacuum fusion and chemical determinations of nitrogen for a large number of zirconium samples. In the analysis of metal of very low gas content, gaseous contamination on the surface of a prepared micro sample could cause an appreciable positive bias, particularly for oxygen, and results that showed the extent of this effect were also quoted.

The Chemical Determination of Nitrogen in Reactor Metals

Mr. J. A. Ryan said that the applicability of the Allen method for the determination of nitrogen in the reactor metals niobium, vanadium, zirconium, molybdenum and beryllium had been demonstrated by comparison of the performance of the method with the Dumas and caustic-fusion methods. Nitrides of the metals had been prepared and used for the comparison experiments. Although the Allen method could be used satisfactorily for all these elements, it could only be used for the determination of nitrogen in molybdenum on a restricted size of sample. The caustic-fusion method was applicable to fully nitrogenated vanadium, but not to samples of vanadium metal, for which it gave "nil" recoveries. No experiments had been carried out with the Dumas method on beryllium, owing to the hazardous toxic nature of the material, but the method could be applied satisfactorily to the other elements.

The Determination of Naturally Occurring Radioactive Impurities in a Uranium Purification Process

Mr. M. R. Hayes said that pitchblende ore contained the radioactive-decay products of uranium in their equilibrium concentrations, and these radioactive impurities were separated from the uranium during the refining process and appeared in the various plant intermediates and residues.

A knowledge of the concentrations of these radioactive impurities was required in order that measures to prevent undue concentration of radioactivity could be taken and to control the disposal of radioactive wastes. Also, as some of the radioactive impurities were valuable by-products in the refining of uranium, analytical control was required to permit them to be recovered efficiently.

Of the twenty-six radioactive isotopes occurring in the ore, the most important were shown to be thorium-230, polonium-210 and radium-226.

The analytical methods used in the determination of these three isotopes were outlined. For thorium-230 and polonium-210, chemical separation followed by alpha counting was used. The methods for radium were purely physical: direct measurement of gamma-ray intensity at the higher levels and separation of radon gas followed by measurement of its activity at lower levels.

The concentrations of these radioactive impurities, and mass balances obtained for them over a period of production, were discussed.

A Simple Manometric Method for the Determination of Carbon in Metals

Mr. M. R. Everett described an apparatus that was simple, compact and portable. It could be used to isolate and determine carbon dioxide in oxygen or nitrogen carrier-gas streams having velocities of up to 300 ml per minute. The sensitivity range was from 10 to 8000 μg of carbon. An efficient multi-loop cold trap isolated the carbon dioxide, which was afterwards expanded at room temperature in a small evacuated calibrated volume that included an atmospheric-column manometer.

SCOTTISH SECTION

A Joint Meeting of the Section and the Methods of Analysis Panel (Glasgow) was held at 7.15 p.m. on Friday, April 25th, 1958, in the Royal College of Science and Technology,

204 George Street, Glasgow, C.1. The Chair was taken by the Chairman of the Methods of Analysis Panel, Mr. J. H. Love.

A lecture on "X-ray Fluorescence Techniques in Analytical Chemistry" was given by E. T. Hall, M.A., D.Phil. (see summary below).

X-ray Fluorescence Techniques in Analytical Chemistry

Dr. E. T. Hall said that the use of X-ray fluorescence both in the laboratory and in process control was an accomplished fact in the United States of America. However, in this country, in spite of the existence of the technique since 1914, the importance of the method was only just being realised.

The speaker gave an outline of the technique together with some idea of how the physical, mechanical and electronic problems had been solved. Reference was made to commercial equipments available, and how automatic servo-controlled spectrometers could carry out automatic analyses of complex systems. Results could be taken either intermittently in digital form or continuously in analogue form.

Some comparisons were made with optical spectrometers, and possible applications to trace analysis were indicated. Examples of suitable problems with their attendant advantages were described. Some mention was also made of the advantages of this technique in non-destructive archaeological analysis of valuable museum objects.

SCOTTISH SECTION and PHYSICAL METHODS GROUP

A Joint Meeting of the Scottish Section and the Physical Methods Group with the Aberdeen University Chemistry Society was held at 7.30 p.m. on Friday, May 16th, 1958, in the Main Lecture Theatre, Chemistry Department, King's College, Old Aberdeen. The Chair was taken by the Chairman of the Physical Methods Group, Mr. R. A. C. Isbell, A.Inst.P.

The following papers were presented and discussed: "The Analysis of Clays Using Ion-exchange Resins," by Mrs. Jean McAuslin, B.Sc., A.R.I.C.; "The Application of Gamma Radiation to the Non-destructive Examination of Coal," by J. Craig Higgins (see summaries below).

During the morning, the Chemistry Department of King's College was open to visitors and there were demonstrations of a cathode-ray polarograph, a Unicam SP900 flame photometer and a high-sensitivity pH meter. In the afternoon, visits were paid to the Macaulay Institute for Soil Research and to the Ministry of Agriculture, Fisheries and Food Experimental Factory.

The Analysis of Clays Using Ion-exchange Resins

Mrs. Jean McAuslin described a method of clay analysis in which the sample was decomposed and the silica removed by treatment with hydrofluoric acid. The metallic constituents of the clay were then separated from one another and determined quantitatively. Iron and manganese were converted to anionic chloride complexes, and aluminium to an anionic phosphate complex. These complexes were then adsorbed on anion-exchange resin columns. A cation-exchange resin column was used to separate sodium and potassium from calcium and magnesium.

Sodium and potassium were determined by flame-photometric methods, and titanium was determined colorimetrically. The remaining elements were determined by titration with ethylenediaminetetra-acetic acid. The behaviour of titanium had been investigated, and provision had been made to prevent its interference in the determination of the other metals.

The Application of Gamma Radiation to the Non-destructive Examination of Coal

Mr. J. C. Higgins said that planning the development of new coalfields required much preliminary proving and survey work. This was carried out to a large extent by exploratory boring. The samples obtained in "core" form from these boreholes provided a valuable cross-section of the coal seams present and their associated strata.

The attenuation by coal of gamma radiation from a radioactive source had been utilised as the basis of an experimental non-destructive method of examining the physical structure of coal seams as provided by these core samples. The method had been used as an aid to the visual assessment of seam structure that was carried out before further physical and chemical tests were made.

The work done so far demonstrated the practicability of the method and showed it to be capable of differentiating between bands of coal that were closely similar in ash content and specific gravity. Sharp resolution of adjacent thin coal and dirt bands was possible and variations in mineral-matter content had been observed in places where they had not been demonstrated by standard preliminary examination.

WESTERN AND MIDLANDS SECTIONS

A JOINT Summer Meeting of the Western and Midlands Sections was held on Friday and Saturday, May 16th and 17th, 1958, in the Lecture Theatre, West Midlands Gas Board, Castle Foregate, Shrewsbury. The Chair was taken on Friday by the Chairman of the Midlands Section, Dr. R. Belcher, F.R.I.C., F.Inst.F., and on Saturday by the Chairman of the Western Section, Mr. S. Dixon. M.Sc.. F.R.I.C.

At 7 p.m. on Friday the following papers were presented and discussed: "The Origins and Growth of Volumetric Analysis" and "The Origins of Quantitative Organic Analysis," by W. I. Stephen, B.Sc., Ph.D., A.R.I.C. At 9.30 a.m. on Saturday the following papers were presented and discussed: "The Historical Development of the Public Analyst," by G. V. James, M.B.E., M.Sc., Ph.D., F.R.I.C., P.A.I.W.E.; "The Origins of Quantitative Chemical Analysis," by R. E. Coulson, F.R.I.C. (see summaries below).

THE ORIGINS AND GROWTH OF VOLUMETRIC ANALYSIS

DR. W. I. STEPHEN described the early history of titrimetry to show how this branch of chemical analysis had played an equally as important part in the development of quantitative analysis as had gravimetry. The contributions of Mohr and Penny to the growth of the subject were also discussed.

THE ORIGINS OF QUANTITATIVE ORGANIC ANALYSIS

DR. W. I. STEPHEN described the contributions of Berzelius, Liebig, Gay-Lussac and Dumas to elemental organic analysis. Subsequent developments in quantitative organic analysis had depended entirely on the work of these famous chemists. Some mention was also made of the history of functional-group analysis.

THE HISTORICAL DEVELOPMENT OF THE PUBLIC ANALYST

DR. G. V. JAMES traced the place of food poisoning and the protection given by select individuals from early times, and described prohibitive legislation in historical times. He mentioned early analytical tests for adulteration, and described the widespread sophistication of the early nineteenth century that led to the *Lancet* Commission and the first Food and Drugs Act of 1860.

Some early books and instruments of this latter period were displayed.

THE ORIGINS OF QUANTITATIVE CHEMICAL ANALYSIS

MR. R. E. COULSON said that Klaproth had laid the foundations of quantitative analysis in his work on minerals. He had shown how even the most refractory materials might be brought into solution and the components separated. Berzelius had extended this work and applied current ideas of the structure of chemical compounds to check the analytical results obtained by himself and others, which had led to a clear understanding of combining proportions.

MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 6.30 p.m. on Wednesday, April 16th, 1958, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

The following paper was presented and discussed: "The Analysis of Silicones and Related Organosilicon Compounds," by J. C. B. Smith.

A JOINT Meeting of the Section with the East Midlands Section of the Royal Institute of Chemistry was held at 7.30 p.m. on Thursday, April 24th, 1958, in the College of Art and Technology, Leicester. The Chair was taken by the Chairman of the East Midlands Section, Dr. A. G. Catchpole, F.R.I.C.

The following paper was presented and discussed: "Developments in the Use of Redox Indicators," by R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F.

BIOLOGICAL METHODS GROUP

An Ordinary Meeting of the Group was held at 6.30 p.m. on Wednesday, April 16th, 1958, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Chairman of the Group, Dr. S. K. Kon, F.R.I.C.

A discussion on "The Mathematics of Sterility Testing" was opened by D. Maxwell Bryce, B.Sc., B.Pharm., F.P.S., A.R.I.C.

Obituary

WILLIAM MACRO SEABER

William Macro Seaber died on March 13th, 1958, after a short illness. He was 75 years of age.

He had been a member of the Society since 1929, and served on the Council in 1939–40.

Having passed the examination for the Bachelor of Science degree of London University, he was also successful in the Institute of Chemistry's examination in Branch E in 1907, and was elected to the Fellowship in 1910. In the same year he commenced his career as a consultant, setting up jointly with the late Maurice Salamon. In 1912 he married Elsie Eleanor Perry, a sister of the late Lord Perry of Stock Havard.

During the first World War he left private practice to go to an explosives works at Hale in Cornwall. In 1919 he left, and, with his wife and two daughters, went to Mexico in the employ of the then Mexican Oil Company, first at the refinery at Minatitlan, and later in Mexico City.

In 1923 he returned to England and purchased the practice of Halse and Marshall. Shortly after this he again entered into partnership with Maurice Salamon. Salamon died in 1928, and Seaber was senior partner in Halse and Marshall and in Salamon and Seaber from that time until his death. He also held a partnership in the firm of John Hughes from 1929 until 1945.

His interest was almost entirely confined to his profession, but within that framework he brought a keen mind and wide experience to the many problems that fascinated him. The papers he published show the width of his interest, and include such titles as "The detection of inflammable and explosive gases in ships' tanks," "Barium as a normal constituent of Brazil nuts," as well as various papers on the determinations of rotenone, carotene and small amounts of bromine.

He was always willing to give practical help to the individual in need, and to give his time and his experience when they were required.

Up to the time of his death he was a member of a number of committees, including the British National Committee of the International Commission for Uniform Methods of Sugar Analysis, the Essential Oils Committee of the British Standards Institution and the Lonchocarpus Panel of the Analytical Methods Committee of the Society for Analytical Chemistry.

R. A. Rabnott

The Determination of Tungsten in Titanium, Zirconium and their Alloys

By D. F. WOOD and R. T. CLARK

(*Research Department, Imperial Chemical Industries Ltd., Metals Division, Kynoch Works, Witton, Birmingham, 6*)

To fulfil the need for satisfactory methods for the determination of tungsten over the range 0·002 to about 1 per cent. in titanium and its alloys, two absorptiometric procedures have been developed, and subsequently extended to the examination of zirconium and its alloys.

A direct procedure, based on the yellow colour produced by the reaction of reduced tungsten with thiocyanate ions, is suitable for the determination of tungsten from 0·05 to 1·6 per cent. in titanium and many of its alloys, and from 0·01 to 1·6 per cent. in zirconium and its alloys; larger amounts can be determined by using a smaller sample weight. The procedure is simple and rapid, and is also suitable for application on a routine basis. Vanadium and molybdenum interfere, and, when these metals exceed specified limits, the toluene-3:4-dithiol procedure is recommended.

A procedure, which depends on the formation of a bluish green complex with toluene-3:4-dithiol, is applicable to the determination of tungsten in both titanium and zirconium-bearing materials over the range 0·002 to 0·8 per cent. Vanadium does not interfere, and interference by molybdenum is overcome by means of a preliminary sulphide separation.

Tungsten may be introduced into titanium, zirconium and their alloys either from the parent ores or by contamination from the tungsten electrodes that are frequently used in the arc-melting of evaluation buttons. Its presence is undesirable because of its considerable hardening effect; further, in zirconium-bearing materials used in nuclear reactors, only small amounts of tungsten (below about 0·005 per cent.) can be tolerated because of its high neutron capture cross-section.

The objective was the determination of tungsten in these materials over the range 0·002 to about 1 per cent.

Colorimetric procedures based on the use of thiocyanate[1,2,3] and toluene-3:4-dithiol (dithiol),[4] commonly used for the determination of tungsten in steel, have been applied to the determination of tungsten in titanium metal,[5,6] and these procedures are at present used in this laboratory.[7]

In the thiocyanate procedure,[5] the sample is dissolved in hydrochloric acid and, in order to obtain reproducible blank values, titanium is completely reduced by boiling the solution with stannous chloride before the addition of thiocyanate. In this procedure, the small absorption of the yellow complex formed between reduced tungsten and thiocyanate ions is measured in the presence of a considerable absorption due to the deep violet colour of titanous chloride, and this limits its application to the determination of tungsten in amounts above about 0·1 per cent. Further, during dissolution in hydrochloric acid, which usually takes several hours, part hydrolysis of titanium sometimes occurs, which results in inconsistent blank values.

In order to extend the application of the thiocyanate procedure, modifications to the published method[5] were examined. These included the use of fluoroboric acid as a solvent; it forms a green-coloured complex fluorotitanate with titanium, and thereby inhibits hydrolysis and minimises blank values, thus allowing the range of the determination to be extended below 0·1 per cent. This acid also expedites dissolution of the metal. It was expected that boiling the solution with stannous chloride would be unnecessary because tungsten would be effectively reduced by titanous ions formed during dissolution of the sample. Application of this modified procedure was extended to titanium alloys and, subsequently, to zirconium and its alloys.

The dithiol procedure depends on the formation of a bluish green complex of tungsten with dithiol and extraction of the complex with *iso*amyl acetate. Although more lengthy than the thiocyanate procedure, it is suitable for the determination of tungsten down to about 0·001 per cent. Examination of titanium - vanadium alloys showed that vanadium

interferes in the dithiol procedure[6] as applied to titanium metal, whereas, in the procedure as applied to steel,[4] it is claimed that vanadium does not interfere.

In order to provide a method for the determination of tungsten below about 0·05 per cent. in titanium alloys, including those containing vanadium, and also in zirconium and its alloys, the dithiol procedure, as applied to steel,[4] was selected as a basis for further investigation.

EXPERIMENTAL

Thiocyanate method for tungsten in titanium

Preliminary experiments—

Initial experiments were made to establish the wavelength at which maximum absorption of the tungsten - thiocyanate complex occurs and then, by using this wavelength, to prepare a calibration graph. The concentrations of hydrochloric acid and ammonium thiocyanate used in these preliminary experiments were those recommended by Bacon.[5]

Absorption curve—A 0·2-g sample of tungsten-free titanium was dissolved in a mixture of 20 ml of hydrochloric acid, sp.gr. 1·18, and 1 ml of fluoroboric acid; 20 ml of sodium tungstate solution (1 ml ≡ 0·1 mg of tungsten) were added and the solution was diluted to 100 ml in a calibrated flask. To a 25-ml aliquot in a 100-ml calibrated flask were added 20 ml (making 25 ml in all) of hydrochloric acid and then 10 ml of 15 per cent. ammonium thiocyanate solution. The solution was diluted to the mark and set aside for 5 minutes at 20° C. Optical-density measurements were then made in 2-cm cells with a Unicam SP600 spectrophotometer. Wavelengths between 3700 and 4500 A were used, and it was found that the maximum absorption is at 4000 A.

This procedure was repeated with a solution containing titanium only, and at 4000 A the absorption, due mainly to fluorotitanate ions, was found to be at a minimum (optical density 0·06).

Calibration graph—Solutions containing 0·2 g of tungsten-free titanium and amounts of sodium tungstate solution (1 ml ≡ 0·1 mg of tungsten) ranging from 0 to 32·0 ml were prepared as before. These were diluted to 100 ml and 25-ml aliquots were taken. The reagents were added as before, the solutions were diluted to 100 ml and the optical densities were measured at 4000 A in 2-cm cells. The prepared calibration graph was linear and was suitable for the determination of tungsten in the range 0·05 to 1·6 per cent.

The blank value (optical density 0·06) due to the green-coloured fluorotitanate ions was equivalent to only half of that obtained in the method described by Bacon.[5] The tendency for titanium to hydrolyse was completely prevented, and tungsten was effectively reduced by titanous ions produced during dissolution of the sample. In addition, the sample dissolved in 10 to 20 minutes, compared with about 2 hours when hydrochloric acid is used alone as recommended.[5]

Effect of various factors—

Because the optical density of the complex decreased over the range 18° to 35° C by 0·0015 per °C rise in temperature, solution temperatures were controlled at 20° ± 1° C while the optical-density measurements were made. Variation in blank values over the same range of temperatures was negligible. The colour was fully developed within 5 minutes of the addition of ammonium thiocyanate solution, and it was stable for about 30 minutes, after which the optical densities slowly decreased, the blank values remaining constant up to 90 minutes after addition of the thiocyanate.

Different amounts of hydrochloric acid between 23 and 40 ml had no effect on the optical density. Below 23 ml, optical densities decreased sharply with decrease in acid concentration; the blank value increased slightly with increase in acid concentration. Different amounts of fluoroboric acid between 0·5 and 2 ml had no effect on the optical density of the complex or on blank values.

Over the range 8 to 20 ml, the amount of 15 per cent. ammonium thiocyanate solution had no significant effect on the optical density, but, below 8 ml, optical densities decreased sharply with decrease in thiocyanate concentration. There was a marked increase in blank values with increase in the amount of thiocyanate from 5 to 20 ml. To ensure full colour development in conjunction with a consistent blank value, 10 ml of ammonium thiocyanate, controlled to within ±0·5 ml, was adequate.

When the procedure was applied to solutions containing titanium in the absence of tungsten, optical densities increased from 0·001 to 0·076 with increase in titanium content over the range 0 to 60 mg, as shown by the following results—

Titanium present, mg	Nil	10	20	30	40	50	60
Optical density	0·001	0·010	0·024	0·038	0·052	0·064	0·076

In blank determinations, therefore, it is essential to use a weight of tungsten-free titanium corresponding to the weight of titanium present in the sample.

Tests on solutions containing 50 mg of titanium and the equivalent of 0·10 and 0·80 per cent. of tungsten, to determine the effect of common alloying constituents and likely impurities, established that no interference was caused by amounts up to at least 20 per cent. of tin or manganese, 10 per cent. of aluminium, 5 per cent. of iron or chromium and 1 per cent. of copper. Molybdenum above 0·25 per cent. caused high results, but interference by molybdenum up to 2 per cent. can be compensated by adding an equivalent amount of molybdenum to the blank solution. Vanadium introduced a positive error, which became significant above about 0·05 per cent.

Thiocyanate method for tungsten in zirconium

Preliminary experiments—

Initial experiments were made to determine the smallest amount of titanium necessary to effect complete reduction of tungsten and then to prepare a calibration graph in the presence of major amounts of zirconium.

Effect of titanium—Samples of tungsten-free zirconium (0·2 g) were dissolved in a mixture of 25 ml of hydrochloric acid, sp.gr. 1·18, and 1 ml of fluoroboric acid. Ten millilitres of sodium tungstate solution (1 ml ≡ 0·1 mg of tungsten) were added, and the solutions were transferred to 100-ml calibrated flasks. Amounts of titanous chloride solution (1 ml ≡ 10 mg of titanium) ranging from 0 to 3 ml were added, followed by 10 ml of 15 per cent. ammonium thiocyanate solution. After dilution to the mark, optical densities were measured at 4000 A in 1-cm cells. Similar tests were made in the absence of tungsten in order to establish blank values. Appropriate blank values were deducted and the results showed that at least 5 mg of titanium^{III} were required for complete reduction of 1 mg of tungsten (see Table I). To

Table I

Effect of titanous chloride solution on the thiocyanate procedure for determining tungsten in zirconium

Each solution contained 0·2 g of zirconium

Tungsten added, mg	Titanous chloride solution added, ml	Optical density	Optical-density difference
Nil	0·0	0·002	
1·0	0·0	0·031	0·029
Nil	0·25	0·003	
1·0	0·25	0·433	0·430
Nil	0·5	0·007	
1·0	0·5	0·621	0·614
Nil	1·0	0·010	
1·0	1·0	0·630	0·620
Nil	2·0	0·018	
1·0	2·0	0·636	0·618
Nil	3·0	0·025	
1·0	3·0	0·644	0·619

provide a reasonable safety margin, 1 ml of this reagent was used in all later experiments; this contributes about 0·01 to the optical density.

Calibration graph—Sodium tungstate solution (1 ml ≡ 0·1 mg of tungsten) in amounts ranging from 0 to 16·0 ml was added to solutions containing 0·2 g of tungsten-free zirconium prepared as before. The reagents were added and the optical densities were measured as before. A satisfactory calibration graph suitable for the determination of tungsten in the range 0·01 to 0·8 per cent. was obtained.

Effect of various factors—

The effects of temperature, acidity, ammonium thiocyanate concentration and stability of the tungsten - thiocyanate complex were studied in the presence of zirconium, and results

agreed with those from similar experiments relating to the determination of tungsten in titanium.

Tests on solutions containing 0·2 g of zirconium and the equivalent of 0·10 and 0·80 per cent. of tungsten established that amounts up to at least 20 per cent. of tin, 5 per cent. of nickel or magnesium and 2·5 per cent. of chromium did not interfere. Copper in excess of 0·5 per cent. interfered, owing to precipitation of cuprous thiocyanate. Iron above about 2·5 per cent. interfered, owing to the yellow colour of ferric ions formed during dissolution of the sample, but interference (up to 5 per cent. of iron) was overcome by increasing the amount of titanous chloride to 2 ml. Molybdenum above 0·05 per cent. caused high results, but interference (up to 0·5 per cent. of molybdenum) was overcome by adding an equivalent amount of molybdenum to the blank solution. Vanadium above 0·01 per cent. interfered.

EXTRACTION OF THE TUNGSTEN - THIOCYANATE COMPLEX—

As a possible means of overcoming interference from alloying amounts of vanadium and molybdenum, and at the same time increasing the sensitivity of the method, attempts were made to extract the complex with organic solvents. Tests with *iso*amyl alcohol, *iso*amyl acetate, hexyl acetate, diethyl ether, chloroform and carbon tetrachloride indicated that only *iso*amyl alcohol extracted the complex to any appreciable extent, but even after four extractions with this solvent it was not completely extracted, and so this possible extension of the procedure was discontinued.

APPLICATION OF THE THIOCYANATE PROCEDURES

The proposed thiocyanate procedures, see p. 331, were applied to samples of titanium, zirconium and their alloys, and, as shown in Table II, reproducible results were obtained.

TABLE II

DETERMINATION OF TUNGSTEN IN SAMPLES OF TITANIUM, ZIRCONIUM AND THEIR ALLOYS

Nominal composition	Tungsten found by thiocyanate method, %	Tungsten found by dithiol method, %
Titanium	—	0·0015, 0·0015
Titanium + 2 per cent. of aluminium + 2 per cent. of manganese	—	0·002, 0·002
Zirconium	—	0·002, 0·002
Zirconium + 1·5 per cent. of tin + 0·1 per cent. of iron + 0·1 per cent. of chromium + 0·05 per cent. of nickel	—	0·002, 0·002
Titanium*	0·44, 0·44, 0·44, 0·445, 0·445, 0·44	0·434, 0·430, 0·435, 0·428, 0·430, 0·430
Titanium + 5 per cent. of aluminium + 2·5 per cent. of tin*	0·16, 0·16	0·170, 0·170
Titanium + 2·5 per cent. of aluminium + 13 per cent. of tin*	0·47, 0·46	0·470, 0·475
Titanium + 6 per cent. of aluminium + 4 per cent. of vanadium*	—	0·425, 0·420
Zirconium + 2·5 per cent. of tin*	0·07, 0·07	0·069, 0·070
Zirconium + 1·5 per cent. of tin + 0·1 per cent. of iron + 0·1 per cent. of chromium + 0·05 per cent. of nickel*	0·40, 0·40, 0·405, 0·40, 0·395, 0·40	0·402, 0·404, 0·404, 0·405, 0·400, 0·395

Standard deviation of thiocyanate method at 0·4 per cent. of tungsten = ± 0·003 per cent.
Standard deviation of dithiol method at 0·4 per cent. of tungsten = ± 0·003 per cent.

* Prepared by an arc-melting process with tungsten electrodes.

DITHIOL METHOD FOR TUNGSTEN IN TITANIUM

A mixture of sulphuric and phosphoric acids, such as that used for dissolving steel, is not suitable for dissolution of titanium because of the insolubility of titanium phosphate; a mixture of sulphuric and fluoroboric acids was therefore used in the experimental work.

PRELIMINARY EXPERIMENTS—

Preliminary experiments were made to establish the wavelength at which maximum absorption of the tungsten - dithiol complex occurs, and then, by using this wavelength, to prepare a calibration graph.

Absorption curve—A 0·25-g sample of tungsten-free titanium was dissolved in a mixture of 50 ml of dilute sulphuric acid (1 + 4) and 0·5 ml of fluoroboric acid, and the solution was oxidised with nitric acid, sp.gr. 1·42. Fifteen millilitres of sodium tungstate solution (1 ml ≡ 0·1 mg of tungsten) were added and, after dilution to 100 ml, a 5-ml aliquot was taken and evaporated to fumes of sulphur trioxide. The solution was cooled, 5 ml of stannous chloride (10 per cent. in hydrochloric acid, sp.gr. 1·18) were added and the solution was heated on a boiling-water bath for 4 minutes. A 10-ml portion of dithiol solution (1 per cent. in *iso*amyl acetate) was added and heating was continued, with frequent shaking, for 10 minutes. The solution was then cooled, transferred to a separating funnel and the aqueous layer removed. The solvent layer was washed twice with diluted hydrochloric acid (4 + 1) and diluted to 50 ml with *iso*amyl acetate in a calibrated flask. The optical density of the solution was determined in a 4-cm cell with a Unicam SP600 spectrophotometer at wavelengths between 5000 and 6600 A; the maximum absorption was found to be at 6300 A.

Calibration graph—Solutions containing 0·25 g of tungsten-free titanium and amounts of sodium tungstate solution (1 ml ≡ 0·1 mg of tungsten) ranging from 0 to 20 ml were diluted to 100 ml. Aliquots of 5 ml were taken and examined as described above, but the optical densities at 6300 A were not proportional to the amounts of tungsten added and colour development was not complete. Further tests with solutions containing tungsten only, and iron in addition to tungsten, indicated that the presence of iron is necessary in order to obtain quantitative values for tungsten.

To investigate the effect of the presence of iron, solutions containing 0·25 g of titanium and the equivalent of 1·5 mg of tungsten were diluted to 100 ml. Five-millilitre aliquots of these solutions, to which were added amounts of ferrous sulphate solution (1 ml ≡ 5 mg of iron) ranging from 0 to 5·0 ml, were examined as before. The optical densities were measured at 6300 A. Increase in the amount of iron over the range 0 to 12·5 mg resulted in an increase in optical density of the tungsten - dithiol complex, but from 12·5 to 25·0 mg of iron there was no significant change in optical density and colour development was complete, as shown by the following results—

Iron present, mg ..	Nil	1·0	5·0	10·0	12·5	15·0	17·5	20·0	25·0
Optical density ..	0·688	0·701	0·712	0·735	0·742	0·748	0·747	0·748	0·749

In all later experiments, 1 ml of ferrous sulphate solution (equivalent to 15 mg of iron) was added to the solutions immediately before evaporation to fumes of sulphur trioxide.

By using this modification, satisfactory calibration graphs were prepared covering the ranges 0·05 to 0·8 per cent. and 0·002 to 0·08 per cent. of tungsten.

EFFECT OF VARIOUS FACTORS—

Tests showed that no significant variation in optical density of the complex occurred over the range 18° to 35° C and strict control of solution temperature during optical-density measurement was therefore not essential. The complex was stable for a period up to 1 hour, after which a decrease in optical density gradually occurred.

In further tests, different amounts of sulphuric acid, sp.gr. 1·84, from 0 to 5 ml had no significant effect on the optical density of the final solution.

Increase in the amount of 10 per cent. stannous chloride solution over the range 2 to 10 ml had, likewise, a negligible effect. Below 2 ml, the optical density decreased with decrease in the stannous chloride concentration, owing to incomplete reduction of the tungsten. Different times of boiling with stannous chloride from 1 to 6 minutes had no effect on the optical density of the complex.

At least 7·5 ml of dithiol solution were required in order to obtain full development of the colour, and no change in the optical density occurred over the range 7·5 to 15 ml. Variation of the time of boiling with this reagent from 3 to 15 minutes had no significant effect.

Tests by the proposed dithiol procedure (see p. 332) established that amounts up to about 20 per cent. of tin, manganese or vanadium, 10 per cent. of aluminium and 5 per cent. of copper, iron, chromium or nickel did not interfere in the determination of 0·02 and 0·60 per cent. of tungsten.

Molybdenum forms a green complex with dithiol under test conditions and this caused serious interference. Molybdenum has not, so far, occurred as a significant impurity in titanium, but it is used as an alloying constituent and the presence of a large amount of this metal had, therefore, to be considered. Attempts to overcome molybdenum interference in the presence of titanium by extraction of the dithiol complex with *iso*amyl acetate before reduction of tungsten, in accordance with a published method for the examination of steel,[4] were unsuccessful and the results were erratic. Results were also erratic when the method of Short[6] was used. High results were attributed to incomplete extraction of molybdenum and low results to extraction of some tungsten during the preliminary separation of molybdenum.

Interference was overcome, however, by precipitation of molybdenum sulphide in acid - tartrate solution. In this method, prior oxidation of the solution with potassium permanganate is necessary, otherwise the results are high, due, presumably, to reduction of molybdenum (by titanous ions) to a lower valency state, which results in incomplete precipitation. The results in Table III show that this procedure can be satisfactorily applied to solutions containing from 0·1 to 10 per cent. of molybdenum, 0·02 to 0·6 per cent. of tungsten and major amounts of titanium.

TABLE III

DETERMINATION OF TUNGSTEN BY THE MODIFIED DITHIOL PROCEDURE FOR USE IN THE PRESENCE OF MOLYBDENUM

Each solution contained 0·25 g of titanium

Molybdenum added, %	Tungsten added, %	Tungsten found, %
0·1	0·02	0·021
1·0	0·02	0·022
10·0	0·02	0·023
0·1	0·05	0·050
1·0	0·05	0·051
10·0	0·05	0·051
0·1	0·60	0·61
1·0	0·60	0·612
10·0	0·60	0·611

DITHIOL METHOD FOR TUNGSTEN IN ZIRCONIUM

Calibration graphs over the range 0·05 to 0·8 per cent. and 0·002 to 0·08 per cent. of tungsten, prepared from solutions also containing 0·25 g of zirconium, were identical with those prepared in experimental work relating to tungsten in titanium.

APPLICATION OF THE DITHIOL PROCEDURE

The dithiol procedure for 0·002 to 0·3 per cent. of tungsten was applied to samples of titanium, zirconium and their alloys and, as shown in Table II, results were reproducible and agreed with those found by the thiocyanate procedures.

METHODS

THIOCYANATE METHOD FOR THE DETERMINATION OF TUNGSTEN IN TITANIUM AND ITS ALLOYS

REAGENTS—

Hydrochloric acid, sp.gr. 1·18.

Fluoroboric acid—To 280 ml of hydrofluoric acid maintained at 10° C add, in small amounts, 130 g of boric acid and stir well. Store in a polythene bottle.

Ammonium thiocyanate solution, 15 per cent.—Dissolve 75 g of ammonium thiocyanate in about 250 ml of water and dilute to 500 ml.

Standard tungsten solution—Dissolve 0·1794 g of sodium tungstate, $Na_2WO_4.2H_2O$, in water and dilute to 1 litre.

1 ml ≡ 0·1 mg of tungsten.

PREPARATION OF CALIBRATION GRAPH FOR 0·05 TO 1·6 PER CENT. OF TUNGSTEN—

Transfer 0·2-g portions of tungsten-free titanium to each of seven beakers and dissolve each portion in 20 ml of hydrochloric acid and 1 ml of fluoroboric acid; warm gently to assist

dissolution. Cool and add, separately, 4·0, 12·0, 16·0, 20·0, 24·0 and 32·0 ml of standard tungsten solution. Use the remaining solution as a blank.

Dilute each solution to 100 ml in a calibrated flask and transfer 25-ml aliquots to separate 100-ml calibrated flasks. Add 20 ml of hydrochloric acid and 10 ml of ammonium thiocyanate solution to each. Dilute to the mark and set them aside for 5 minutes at 20° ± 1° C.

Measure the optical density of each at a wavelength of 4000 A in 2-cm cells.

PROCEDURE—

Determine a blank value by using a weight of tungsten-free titanium corresponding approximately to the weight of titanium in the sample.

Dissolve a 0·2-g sample in 20 ml of hydrochloric acid and 1 ml of fluoroboric acid; warm gently to assist dissolution. (For amounts of tungsten in excess of 1·6 per cent. up to 3·2 per cent., use a smaller weight of sample.) Cool, dilute to 100 ml in a calibrated flask and proceed as described for the preparation of the calibration graph.

Calculate the tungsten content of the sample from the calibration graph.

Note that vanadium above about 0·05 per cent. and molybdenum above about 0·25 per cent. introduce significant positive errors. Molybdenum (up to about 2 per cent.) can be corrected for by adding an equivalent amount of molybdenum to the blank solution. For samples containing vanadium or molybdenum in excess of these limiting amounts, the dithiol method is recommended.

THIOCYANATE METHOD FOR THE DETERMINATION OF TUNGSTEN IN ZIRCONIUM AND ITS ALLOYS

REAGENTS—

The reagents used are the same as for the determination of tungsten in titanium, *plus*—

Titanous chloride solution—Dissolve 1·0 g of titanium in about 50 ml of hydrochloric acid, sp.gr. 1·18. Cool and dilute with hydrochloric acid to 100 ml. This reagent must be freshly prepared.

PREPARATION OF CALIBRATION GRAPH FOR 0·01 TO 0·8 PER CENT. OF TUNGSTEN—

Transfer 0·2-g portions of tungsten-free zirconium to each of seven beakers and dissolve each portion in 25 ml of hydrochloric acid and 1 ml of fluoroboric acid; warm gently to assist dissolution. Cool and add, separately, 2·0, 4·0, 6·0, 8·0, 12·0 and 16·0 ml of standard tungsten solution. Use the remaining solution as a blank.

Transfer each solution to a 100-ml calibrated flask, washing with about 25 ml of water. Add 1 ml of titanous chloride solution and 10 ml of ammonium thiocyanate solution to each Dilute to the mark and set them aside for 5 minutes at 20° ± 1° C.

Measure the optical density of each at a wavelength of 4000 A in 1-cm cells.

PROCEDURE—

Determine a blank value on the reagents with each batch of samples.

Dissolve a 0·2-g sample in 25 ml of hydrochloric acid and 1 ml of fluoroboric acid; warm gently to assist dissolution. (For amounts of tungsten in excess of 0·8 per cent. up to 3·2 per cent., use a smaller weight of sample. When the tungsten content is below 0·05 per cent., use 4-cm cells.) Cool and transfer the solution to a 100-ml calibrated flask with about 25 ml of water, and then continue as described for the preparation of the calibration graph.

Calculate the tungsten content of the sample from the calibration graph.

Note that vanadium above about 0·01 per cent. and molybdenum above about 0·05 per cent. introduce significant positive errors. Molybdenum (up to about 0·5 per cent.) can be corrected for by adding an equivalent amount of molybdenum to the blank solution. For samples containing vanadium or molybdenum in excess of these limiting amounts, the dithiol method is recommended.

DITHIOL METHOD FOR THE DETERMINATION OF TUNGSTEN IN TITANIUM, ZIRCONIUM AND THEIR ALLOYS

REAGENTS—

Sulphuric acid, dilute (1 + 4)—To 400 ml of water, add 100 ml of sulphuric acid, sp.gr. 1·84. Mix well and cool.

Fluoroboric acid—Prepare as described on p. 331.

Nitric acid, sp.gr. 1·42.

Iron solution—Dissolve 1·5 g of electrolytic iron in 25 ml of dilute sulphuric acid (1 + 4) and dilute to 100 ml.

1 ml ≡ 0·015 g of iron.

Stannous chloride solution, 10 per cent. w/v—Dissolve 10 g of stannous chloride, $SnCl_2.2H_2O$, in 100 ml of hydrochloric acid, sp.gr. 1·18

Dithiol solution—Dissolve 1 g of toluene-3:4-dithiol in 100 ml of *iso*amyl acetate.

Hydrochloric acid, diluted (4 + 1)—Dilute 400 ml of hydrochloric acid, sp.gr. 1·18, with 100 ml of water.

Standard tungsten solution—Dissolve 0·1794 g of sodium tungstate, $Na_2WO_4.2H_2O$, in water and dilute to 1 litre. For use, dilute 100 ml of this solution to 1 litre.

1 ml ≡ 0·01 mg of tungsten.

PREPARATION OF CALIBRATION GRAPHS—

Dissolve 0·625 g of tungsten-free metal (titanium or zirconium) in 125 ml of dilute sulphuric acid (1 + 4) and 1 ml of fluoroboric acid; warm gently to assist dissolution and then oxidise with a few drops of nitric acid. Boil to remove nitrous fumes, cool and dilute to 250 ml in a calibrated flask.

Calibration graph for 0·05 to 0·8 per cent. of tungsten—Transfer five 5-ml aliquots of the solution (titanium or zirconium) to each of five 100-ml conical flasks and add, separately, 2·5, 5·0, 7·5 and 10·0 ml of standard tungsten solution. Use the remaining solution as a blank.

Add 1 ml of the iron solution to each and evaporate to fumes of sulphur trioxide. Cool, add 5 ml of stannous chloride solution to each, place them on a boiling-water bath and agitate at frequent intervals over 4 minutes. Add 10 ml of dithiol solution and continue heating on the water bath, with frequent agitation, for 10 minutes. Cool to about 30° C and transfer each solution to a separating funnel, rinsing with three 2-ml portions of *iso*amyl acetate. Shake and allow the layers to separate; run off and discard each lower acid layer. Wash the solvent layers twice with 10-ml portions of diluted hydrochloric acid (4 + 1) and each time discard the lower acid layers.

Remove the upper solvent layers containing the tungsten, and transfer them to 50-ml calibrated flasks that have previously been washed free from water with ethanol and then with *iso*amyl acetate. Dilute each solution to the mark with *iso*amyl acetate and mix well.

Measure the optical density of each solution at a wavelength of 6300 A in 4-cm cells.

Calibration graph for 0·002 to 0·08 per cent. of tungsten—Transfer five 25-ml aliquots of the solution (titanium or zirconium) to each of five 100-ml conical flasks and add, separately, 1·25, 2·5, 3·75 and 5·0 ml of standard tungsten solution. Use the remaining solution as a blank.

Add 1 ml of the iron solution to each and continue as described for the preparation of the calibration graph for 0·05 to 0·8 per cent. of tungsten, but transfer the final *iso*amyl acetate layers containing the tungsten to 25-ml calibrated flasks washed free from water.

Dilute each to the mark with *iso*amyl acetate and continue as previously described.

PROCEDURE FOR 0·002 TO 0·8 PER CENT. OF TUNGSTEN—

Dissolve a 0·25-g sample in 50 ml of dilute sulphuric acid (1 + 4) and 0·5 ml of fluoroboric acid; warm gently to assist dissolution and oxidise with a few drops of nitric acid. Boil to remove nitrous fumes, cool and transfer to a 100-ml calibrated flask and dilute to the mark. Transfer 5 ml of the solution to a 100-ml conical flask, add 1 ml of the iron solution and continue as described for the preparation of calibration graph for 0·05 to 0·8 per cent. of tungsten.

Calculate the tungsten content of the sample from the calibration graph.

If the tungsten content of the sample is below 0·05 per cent., transfer a 25-ml aliquot from the remainder of the 100 ml of solution to a 100-ml conical flask, add 1 ml of the iron solution and continue as described for the preparation of the calibration graph for 0·002 to 0·08 per cent. of tungsten.

PROCEDURE FOR TUNGSTEN IN SAMPLES CONTAINING MOLYBDENUM—

Dissolve a 0·25-g sample in 25 ml of dilute sulphuric acid (1 + 4) and 0·5 ml of fluoroboric acid; warm gently to assist dissolution and oxidise by dropwise additions of a saturated solution of potassium permanganate, until a permanent brown precipitate is present. Add

sulphurous acid dropwise until the precipitate has dissolved and then boil for 2 minutes to remove excess of sulphur dioxide. Add 15 ml of 50 per cent. tartaric acid solution, 250 ml of water and warm to 80° C. Pass a rapid stream of hydrogen sulphide through the solution for 30 minutes and then allow to cool to room temperature.

Transfer the solution and precipitate to a 500-ml calibrated flask and dilute to the mark. Filter an approximately 50-ml portion through a Whatman No. 42 filter-paper, transfer 25 ml of the filtrate to a 100-ml conical flask, add 1·0 ml of dilute sulphuric acid (1 + 4) and 1 ml of the iron solution and then evaporate to fumes of sulphur trioxide.

Destroy carbonaceous matter by adding nitric acid, sp.gr. 1·42, in 2-ml portions to the hot residue. Continue as described for the preparation of the calibration graph for 0·05 to 0·8 per cent. of tungsten.

Calculate the tungsten content of the sample from the calibration graph.

If the tungsten content of the sample is below 0·05 per cent., transfer a 100-ml aliquot of the filtrate to a 250-ml conical flask, add 1·5 ml of sulphuric acid, sp.gr. 1·84, and 1 ml of the iron solution and then evaporate to fumes of sulphur trioxide. Destroy carbonaceous matter and continue as described for the preparation of the calibration graph for 0·002 to 0·08 per cent. of tungsten.

CONCLUSIONS

The proposed absorptiometric thiocyanate procedure is satisfactory for the determination of 0·05 to 1·6 per cent. of tungsten in titanium and many of its alloys. Vanadium above 0·05 per cent. and molybdenum above 0·5 per cent. interfere. Interference by molybdenum, up to about 2 per cent., can be overcome by adding an equivalent amount of molybdenum to the blank solution. The proposed thiocyanate procedure for the examination of zirconium and its alloys is applicable over the range 0·01 to 1·6 per cent. of tungsten. Vanadium above 0·01 per cent. and molybdenum above 0·05 per cent. interfere. Interference by molybdenum, up to 0·5 per cent., can be compensated for. Both procedures can be extended to the determination of tungsten up to about 3·2 per cent. by using a smaller weight of sample. The procedures are simple, rapid and particularly suitable for control analysis.

The dithiol procedure is suitable for the determination of tungsten in the range 0·002 to 0·8 per cent. in titanium, zirconium and their alloys. By using smaller absorption cells, it can be extended to the determination of amounts of tungsten up to about 3·2 per cent. The presence of iron is necessary in order to obtain quantitative results.

Vanadium does not interfere, and interference by molybdenum can be overcome by incorporating a preliminary precipitation of molybdenum sulphide. The dithiol method is more time-consuming than the thiocyanate method and is, therefore, only recommended in the examination of samples containing amounts of vanadium or molybdenum sufficient to cause interference with the thiocyanate procedure, and for general application to materials containing less than about 0·05 per cent. of tungsten.

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The Determination of Chlorinated Hydrocarbon Pesticide Residues in Plant Material

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A method is described for the determination of a number of chlorinated hydrocarbon pesticide residues in plant material. After extraction and partial purification, the residues are analysed for total organic chlorine by a modified Stepanow procedure, followed, after the removal of organic matter and excess of sodium ions, by a volumetric determination of chloride by the mercuric oxycyanide method.

PROCEDURES for the determination of organic chlorine that involve reduction with sodium by modifications of the original Stepanow method[1] have frequently been published, and that described in a recent report of the Analytical Methods Committee of the Society for Analytical Chemistry[2] is a typical application. *iso*Propyl alcohol is now the usual medium for the reduction, although *iso*butyl[3] and *iso*amyl[4] alcohols and a mixture of dioxan and ethanolamine[5] have also been used. In this paper a further modification of the Stepanow method is described, together with its application on the semi-micro scale to the determination of chlorinated hydrocarbon pesticide residues in plant material.

The rapid decomposition of organic halogen compounds by reaction with aromatic sodium compounds has been utilised by Liggett[6] and others,[7,8] and is especially advantageous in the analysis of volatile materials, as the reaction proceeds rapidly even in the cold. Reagents such as sodium diphenyl and sodium naphthalene are, however, troublesome to prepare and store, and, in the proposed application of the reaction, sodium naphthalene is generated directly in the reaction flask instead of being added as a prepared reagent. The resulting technique resembles that of Stepanow, but is much more rapid, partly because the end-point of the reaction is self-indicating.

From the limited range of solvents in which the formation of aromatic sodium compounds readily takes place, tetrahydrofuran was selected in preference to 1:2-dimethoxyethane. Two other solvents of interest noted in the course of the work were *iso*propylamine and *n*-butylamine. The velocity of the reaction increases markedly with the concentration of the aromatic compound, in this instance naphthalene, and it is therefore desirable to keep the volume of solvent as small as possible.

The modified Stepanow procedure described later is satisfactory for the semi-micro determination of amounts of organic chlorine up to at least 10 mg. The end-point of the reaction, which is indicated by the intense green colour of excess of sodium naphthalene, may become less apparent with the larger amounts of chlorine, as the reacting solution often becomes deeply coloured. Gravimetric determination of chlorine as silver chloride was preceded by part neutralisation of the reaction solution, evaporation to dryness in a platinum basin and gentle ignition to remove all traces of organic matter. The part removal of organic matter by means of an ether separation gave very low results in the analysis of a chlorinated nitro compound, owing to incomplete precipitation of silver chloride.

Application of the proposed method to pesticide residues was intended to attain a sensitivity of 10 μg or less of chlorine, and a volumetric finish by the mercuric oxycyanide method[9,10] was adopted, as this is simple and, on the semi-micro scale, sufficiently sensitive. To achieve a reasonably sharp end-point in the titration of chloride at high dilutions, it is necessary to remove both the excess of sodium ions, by means of a cation-exchange resin, and, by careful ignition, all traces of organic matter.

The extraction with light petroleum of chlorinated hydrocarbon pesticides, added in known amounts to plant material, gave low yields and was abandoned in favour of extraction with a mixture of equal volumes of light petroleum and acetone. Benzene, which is often recommended, has the disadvantage of not being readily removed in a Danish - Kuderna evaporator. The excellent penetrating power for plant tissues possessed by the solvent mixture gives rise to extracts containing considerable amounts of plant extractives, and some degree of chromatographic separation is generally desirable. Activated alumina of suitably controlled water content can be used to effect a part separation of plant colouring

matter without retention, after elution with light petroleum, of any of a number of chlorinated hydrocarbon pesticides tested, with the exception of Kelthane, which is rather strongly adsorbed.

The method is not intended for the analysis of materials that have an appreciable fat content. Although it does not appear to be practicable to separate a wide range of the chlorinated pesticides from large amounts of fat by a single method, techniques of limited application have been described,[11,12,13,14] and a combustion method of analysis has recently been recommended in this connection.[15]

Method of extracting the pesticide

Apparatus—

Machine for sub-dividing the sample material—A domestic mincing machine of large capacity.

Extraction vessels—Flat-bottomed 500-ml or larger flasks with standard ground-glass stoppers held in position by spring clamps. A wide socket, such as a B34, is desirable to facilitate the introduction of the sample material. Before insertion of the stopper, the ground-glass surfaces should be carefully cleaned and the stopper wetted with water to improve the seal.

Shaking machine—This should rotate the extraction vessels with an end-over-end motion at a rate of about 1 revolution per second.

Reagents—

Light petroleum, redistilled—The fraction boiling over the range 60° to 80° C.

Acetone, redistilled.

Procedure—

Introduce 100 to 300 g of the minced or shredded sample into the extraction vessel and, for each gram of material, add 1 ml of light petroleum, accurately measured, and 1 ml of acetone. For fibrous absorbent materials, such as grass, these volumes need to be doubled. Insert the stopper, rotate the flask for 1 hour and then pour the liquid through a fast-filtering paper into a separating funnel. Run off and reject any lower aqueous layer and to the remainder add an equal volume of distilled water. Wash the extract free from acetone and water-soluble chloride by shaking first with this and then with two further similar portions of distilled water. Run off the final water washings, add a few grams of anhydrous sodium sulphate and then shake to absorb the remaining water. Run off the liquid into a measuring cylinder and note the volume of light petroleum recovered, or remove by pipette an aliquot calculated to contain not more than 1·5 mg of chlorine. The pesticide is assumed to be distributed uniformly in the total original volume of light petroleum.

Method of treating the extract

Apparatus—

Chromatographic tube—A filter tube, 30 mm × 200 mm, with a No. 1 sintered-glass plate.

Evaporator—A simple form of Danish - Kuderna evaporator.[16] This consists of a 500-ml round-bottomed flask, the neck of which is fitted with a B24 ground-glass socket, and to the bottom of which is sealed a B14 ground-glass cone. In use, a splash head joined to a condenser for solvent recovery is fitted to the socket, and a 25-ml round-bottomed flask with a B14 ground-glass socket is attached to the cone and held in place by a spring clamp. The ground-glass joints are moistened with liquid paraffin before assembly and the apparatus is heated by supporting the larger flask on an open-ended cylinder, *e.g.*, made from a tin can, that stands on a steam-bath in such a way that the 25-ml flask and the lower part of the larger flask are surrounded by steam. Some device to prevent bumping of the liquid is necessary, and for this purpose a narrow strip of polytetrafluoroethylene sheeting was found to be effective.

Reagents—

Activated alumina—Heat dry aluminium hydroxide to 800° C and maintain at this temperature for not less than 1 hour; when cool, transfer the ignited material to a stoppered bottle, add 5 per cent. w/w of water and set aside overnight. Shake to mix the prepared alumina before use.

Sodium sulphate, anhydrous.

Light petroleum, redistilled—The fraction boiling over the range 60° to 80° C.

PROCEDURE—

Transfer 10 g of activated alumina to the chromatographic tube and tap down to ensure that the column is uniformly packed. Cover the alumina with a 1-cm layer of sodium sulphate and arrange to collect the effluent from the column in the evaporator. Introduce the extract carefully, so as not to disturb the column, and, when it has passed completely through the column, add light petroleum rinsings; allow these to drain, and complete the operation by washing the column with 100 ml of light petroleum.

Place the evaporator on a steam-bath after adding to the contents 2 drops of liquid paraffin and, when the volume of liquid has been reduced to a few millilitres, remove the evaporator and allow it to cool. Take off the splash head and rinse the apparatus with light petroleum. Detach the 25-ml flask and continue the evaporation on a water bath at 40° C with a stream of dry air until the remaining solvent has been removed.

MODIFIED STEPANOW METHOD FOR THE DETERMINATION OF ORGANIC CHLORINE

APPARATUS—

Reflux condenser—A small Liebig condenser fitted with a B14 ground-glass cone.

Agla micrometer-syringe pipette—A right-angled glass jet is required. A suitable jet can be readily made from drawn-out glass tubing and attached to the syringe by a short piece of capillary plastic or rubber tubing, the flexibility of which protects the jet against accidental breakage or dislocation.

Magnetic stirrer.

Silica basins—Between determinations these should be kept filled with chromic acid cleaning mixture.

REAGENTS—

Naphthalene—Analytical-reagent grade.

Tetrahydrofuran—Purify by placing 20 ml in a 200-ml flask fitted with a reflux condenser by means of a ground-glass joint, and add 4 g of naphthalene and 4 g of clean sodium cut into small pieces. Boil the liquid until it becomes dark green, and then for a further 5 minutes. Continue boiling, and, by way of the condenser, add from a dropping funnel a further 100 ml of tetrahydrofuran and then 20 ml of xylene, the additions being made at such a rate that the colour of the solution is not discharged. Finally, replace the reflux condenser by an ordinary condenser with the addition of a fractionating column and distil off the purified tetrahydrofuran, which should be stored away from light.

Sodium—To prepare the sodium in a convenient form for use, clean a number of pellets in turn by immersion in *iso*propyl alcohol and warming on a steam-bath until a vigorous reaction is proceeding. Quickly rinse the pellets with light petroleum and transfer them to a nickel crucible containing liquid paraffin. Heat the pellets until they melt, and then stir gently to assist coagulation into a large globule. Draw up the molten metal into clean dry glass tubes of about 5 mm internal diameter and 300 mm long, wetted internally with liquid paraffin. Allow the tubes to cool thoroughly, and extrude the sodium as required with the help of a glass rod.

iso*Propyl alcohol, diluted* (1 + 1)—Add 1 volume of analytical-reagent grade *iso*propyl alcohol to 1 volume of distilled water.

Screened methyl red indicator solution—Dissolve 0·08 g of water-soluble methyl red in 25 ml of distilled water, and 0·02 g of methylene blue in 25 ml of ethanol. Mix equal volumes of the two solutions for use.

Sulphuric acid, 0·1 N, and approximately 0·04 N—A 0·1 *N* solution of sulphamic acid can alternatively be used; prepare an aqueous solution containing 0·971 g of the pure recrystallised acid per 100 ml.

Potassium hydroxide solution—An approximately 0·04 *N* solution of the analytical-reagent grade material.

Mercuric oxycyanide reagent solution—Dissolve 4 g of mercuric oxycyanide in 100 ml of distilled water, stirring on a steam-bath to assist dissolution. Cool and filter the solution, which is slightly alkaline and must be neutralised. For this purpose, carry out the titration procedure described later for chloride determination on 15 ml of distilled water, and thereby

determine the volume of 0·1 *N* acid required to neutralise 2 ml of the mercuric oxycyanide reagent under the conditions of the titration. Hence calculate the volume of acid to be added to neutralise the remaining bulk of the reagent.

Ion-exchange resin—Introduce 10 ml of dry Zeo-Karb 225, (40 to 60-mesh) in the hydrogen form, into a glass tube of 16 mm internal diameter and 150 mm long, which tapers at the lower end to a jet and is fitted with a retaining plug of cotton-wool. Regenerate the resin before use and after each determination by running through the column, successively, 15 ml of acetone, 15 ml of diethyl ether, 15 ml of 10 per cent. v/v nitric acid and, finally, not less than 40 ml of distilled water. The resin can be used many times.

If distilled water from the regular supply is found to contain significant amounts of chloride, it should be made alkaline and redistilled.

PROCEDURE—

To the residue in the 25-ml flask add approximately 0·4 g of naphthalene, 1·5 to 2 ml of purified tetrahydrofuran and 0·2 g of sodium cut into small pieces. Attach the reflux condenser, which should be quite dry, and boil the liquid over the flame of a microburner, *e.g.*, the jet of a bunsen burner, until the appearance of an intense dark green colour indicates the end of the reaction, usually after from 2 to 5 minutes in the absence of appreciable amounts of moisture. Continue heating and add 2 ml of diluted *iso*propyl alcohol drop by drop. When all the residual sodium has dissolved, remove the flask and add distilled water to a total volume of about 15 ml.

Cool the flask in ice, then pour the contents into the resin column and collect the effluent in a silica basin. When all the liquid has entered the resin, rinse the flask with about 20 ml of distilled water and add the washings to the column. When the column has drained wash the resin with a further 20 ml of distilled water. To the combined effluent and washings add phenolphthalein indicator and 0·04 *N* potassium hydroxide until just alkaline. Evaporate the liquid to dryness under an infra-red lamp, and then heat the basin, held in tongs over the flame of a bunsen burner, to a temperature just short of redness. It is essential to carbonise organic matter completely, but neither necessary nor desirable to attempt to burn off all the residual carbon. Cool the basin and add about 5 ml of distilled water and 1 drop of screened methyl red indicator solution. Stir the solution and make it just acid with 0·04 *N* sulphuric acid, then place the basin on a steam-bath for 1 to 2 minutes, with occasional stirring and further additions of acid if the solution turns alkaline. Transfer the solution to a 25-ml beaker, rinse the basin with distilled water and add the washings to the beaker until the total volume is approximately 15 ml.

Cool the solution to room temperature and place the beaker on a magnetic stirrer. Add 4 drops of screened methyl red indicator solution and 0·04 *N* potassium hydroxide until the solution is just alkaline, and then standard 0·1 *N* acid from the micrometer-syringe pipette to give a persistent pinkish grey tint. Add 2 ml of mercuric oxycyanide reagent solution and titrate with the acid to the same end-point colour.

Determination of titration factor—Prepare an aqueous solution of potassium chloride containing 100 μg of chlorine per ml. Place aliquots up to 10 ml of this solution in a series of 25-ml beakers and dilute each to 15 ml with distilled water. Carry out the titration on each aliquot, and on 15 ml of distilled water, in the way described above. Plot graphically micrograms of chlorine taken against micrometer-reading differences less that for the distilled water titration. The relationship is not strictly stoicheiometric, but should be substantially linear over this range. Hence calculate the titration factor in micrograms of chlorine per millimetre on the micrometer scale.

Determination of the blank value—Carry out a blank determination to ascertain the correction to be applied for chlorine present in the reagents. With reagents of reasonable purity and a laboratory atmosphere free from chloride fumes, this correction should not be more than 10 μg.

RESULTS

As sample material known to be uncontaminated with pesticide was not conveniently obtainable, and the concentration of any natural organic chlorine was uncertain, cabbage and tomato samples were minced and the minced material was well mixed and divided into halves. One half of each sample was treated as a control and a known weight of pesticide

was added to the other half in the form of a solution in light petroleum, which was allowed to evaporate.

The results in Table I represent over-all recoveries of the various pesticides after deduction of the equivalent of any organic chlorine found in the control samples, and are calculated on the theoretical chlorine contents of the pure crystalline substances and on the chlorine content of the technical materials as determined by analysis.

TABLE I

RECOVERY OF PESTICIDES ADDED TO PLANT MATERIAL

Pesticides were added in the pure crystalline forms, except chlordane and toxaphene, which were added as the technical products

Pesticide	Pesticide found, p.p.m.	Organic chlorine in control, p.p.m.
With 1 *mg of pesticide added to* 100 *g of minced cabbage*, i.e., 10 *p.p.m. of pesticide*—		
γ-Hexachlorocyclohexane ..	9·8, 9·4	0·05, 0·05
pp'-DDT	9·8, 9·8	0·05, Nil
Methoxychlor	9·0, 8·8	0·35, Nil
Aldrin	9·6, 9·6	0·05, Nil
Dieldrin	9·2, 9·8	Nil, Nil
Endrin	9·4, 9·9	Nil, 0·2
Chlorbenside	9·9, 9·4, 9·5	Nil, 0·15, 0·05
Chlordane	8·7, 9·2	Nil, 0·05
Toxaphene	9·6, 10·3	0·05, Nil
With 1 *mg of pesticide added to* 100 *g of minced tomato*, i.e., 10 *p.p.m. of pesticide*—		
γ-Hexachlorocyclohexane ..	10·0, 10·1	0·05, 0·05
pp'-DDT	10·7, 9·9	0·05, 0·05
Chlorbenside	10·0, 10·4, 10·2	0·1, 0·2, 0·05
Toxaphene	10·1, 10·3	0·25, 0·05
With 250 μg *of pesticide added to* 250 *g of minced cabbage*, i.e., 1 *p.p.m. of pesticide*—		
Aldrin	0·91, 0·91, 0·95	0·12, 0·08, 0·08
Dieldrin	0·97, 0·85, 0·90	0·08, 0·14, 0·14
Endrin	1·09, 0·83, 0·67	0·14, 0·02, Nil

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The Determination of DDT in Plant Materials and Soil

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Two procedures, based upon nitration and colour formation with ethanolic potassium hydroxide solution, are described for the determination of DDT in foliage, fruits, grain and soil. In the first, DDT is determined within the range 0 to 350 μg, and in the second, within the range 0 to 30 μg. Interference by wax and pigments is overcome by treatment with alumina and oxidation with acidified permanganate, or by oxidation with acidified permanganate alone.

In work on the chemical control of plant pests and diseases, methods were required for the examination of spray deposits in the assessment of spraying efficiency. Progress reports have been made on the development of techniques for the determination of copper,[1] sulphur,[2] captan (N-trichloromethylthio-4-*cyclo*hexene-1:2-dicarboxyimide),[3] DDT [1:1:1-trichloro-2:2-di(*p*-chlorophenyl)ethane],[4,5] chlorobenzilate (ethyl 4:4′-dichlorobenzilate)[6] and of DDT and chlorbenside (*p*-chlorobenzyl *p*-chlorophenyl sulphide) occurring together.[7]

Two procedures have been used for the determination of DDT in spray deposits. The first, called for convenience the macro method, is designed for the analysis of comparatively large samples of fresh foliage (10 g), fruits or grain (50 g) or soil (20 g), and DDT can be determined when present in amounts within the range 0 to 350 μg. The second, a rapid micro method used in studies of the distribution of the insecticide over plants, is suitable for the analysis of single small fruits or samples of between 0·1 and 0·5 g of foliage or 5 g of grain or soil. In this method, the range of DDT covered is 0 to 30 μg. Both procedures are based upon those of Schechter, Soloway, Hayes and Haller[8] and Illing and Stephenson,[9] in which DDT, extracted from plant tissue with a suitable solvent, is nitrated and a colour is formed with sodium methylate or ethanolic alkali. Amsden and Wallbridge[10] propose the use of *iso*propylamine for colour formation after nitration.

Experimental

Macro method of extracting the DDT—

Foliage and fruits—An extraction procedure was used to assess the extent to which DDT could penetrate into plant tissue. To obtain the surface deposits, leaves and fruits were washed four times with carbon tetrachloride at room temperature. Most of the DDT was recovered in the first two washings; none was found in the fourth washing. The plant material was then dried in air, powdered and extracted by hot percolation with carbon tetrachloride, when additional amounts of DDT equivalent to 10 to 20 per cent. of the total deposits on the leaves were recovered.[4] No absorbed DDT was detected in fruits such as blackcurrants and grapes. The ability of DDT to penetrate into foliage should be borne in mind in the analysis of leafy crops.

Carbon tetrachloride was preferred as solvent since it removes the DDT with a minimum amount of pigment and gives no interference in the nitration procedure.

Grain—The grain was percolated for 30 minutes with hot carbon tetrachloride.

Soil—An examination was made of sandy loam soil samples (pH 6·2 to 6·4 and containing 2·5 per cent. of organic matter) in which DDT had been incorporated. The soil was prepared for analysis by drying in air and passage through a $\frac{1}{8}$-inch square-hole sieve. Extraction was carried out on 20-g portions in three successive stages: (*a*) by hot percolation with carbon tetrachloride, (*b*) by setting the soil aside overnight in a (2 + 1) mixture of carbon tetrachloride and *iso*propyl alcohol, and (*c*) by hot percolation with *iso*propyl alcohol. Samples were also examined by direct hot percolation with acetone or *iso*propyl alcohol. The results of analysis showed that the treatment with carbon tetrachloride failed to extract all the DDT. Extraction with carbon tetrachloride and then *iso*propyl alcohol gave values that agreed closely with those obtained with acetone or *iso*propyl alcohol alone.[5]

Micro method of extracting the DDT—

Foliage and fruits—Because small amounts of plant tissue were used, no attempt was made to distinguish between surface and absorbed deposits. Acetone was used as the solvent

to obtain the total deposits, five leaf discs, each of 1-cm diameter, or single small fruitlets being extracted by hot percolation for 15 minutes.

Grain—Some 5-g samples of grain were extracted by hot percolation with acetone for 15 minutes.

Soil—Tests showed that the recoveries of DDT from a sandy loam soil after extraction with acetone of 5 or 20-g samples agreed well with those after extraction with *iso*propyl alcohol.[5]

MACRO METHOD OF REMOVING INTERFERENCE BY WAX AND PIGMENTS—

The carbon tetrachloride extracts of foliage, fruits and grain were passed through a column of activated alumina to remove pigments and most of the wax. This treatment also effectively removed interfering wax and pigments from extracts of light soils; some soils rich in organic matter and some samples of grain gave highly pigmented solutions, and for these oxidation with acidified potassium permanganate was required after passage through the alumina column.

MICRO METHOD OF REMOVING INTERFERENCE BY WAX AND PIGMENTS—

The complete removal of interference by pigments and fatty material extracted by the acetone was necessary to obtain significant values for DDT over the range 0 to 30 μg. This was achieved without loss of DDT by oxidation with potassium permanganate in dilute acetic acid.

NITRATION OF THE DDT—

Tests showed that, after removal of most of the wax, nitration at 100° C was completed in 10 minutes and this period of heating was adopted for both methods. Under the conditions of the test, the product formed is the tetranitro derivative, 1:1:1-trichloro-2:2-di(4-chloro-3:5-dinitrophenyl)ethane.

SEPARATION OF THE NITRATED DDT—

Separation of the nitrated DDT can be effected by extraction with ether, benzene, carbon tetrachloride or any other suitable solvent.

In the macro method, we have preferred carbon tetrachloride, which occludes less water than ether and ensures fewer manipulations than when benzene is used. The nitrated DDT has a low solubility in carbon tetrachloride, but with the procedure recommended, which involves extraction from an aqueous solution saturated with salts, the recovery of the nitro-DDT is complete. In the micro method, benzene has been used as solvent for the extraction of the nitro compound.

COLOUR FORMATION—

Schechter, Soloway, Hayes and Haller[8] recommended the use of sodium methylate solution, standardised at 10 $\pm$ 0·1 per cent., to form a colour with the nitro-DDT in benzene solution. We used ethanolic potassium hydroxide,[9] which forms a blue colour with the nitrated DDT in carbon tetrachloride (macro method) or benzene (micro method). The maximum development of colour occurs after 5 minutes. The concentration of potassium hydroxide is not critical, colours of equal intensity being given over the range 3·5 to 6·5 per cent.[4]

METHOD

REAGENTS—

Carbon tetrachloride—Fractionated before use.
Acetone—Fractionated before use.
Benzene—Fractionated before use.
Acetic acid, glacial.
Potassium permanganate solution—A 2·5 per cent. aqueous solution.
Sodium metabisulphite solution—A freshly prepared 5 per cent. aqueous solution.
Aluminium oxide for chromatographic analysis.
Nitration acid—Prepared by mixing equal volumes of fuming nitric acid and concentrated sulphuric acid.
Potassium hydroxide solution, 4 N.
Sodium sulphate, anhydrous.

Ethanolic potassium hydroxide solution—Prepared by heating 5 g of potassium hydroxide with 100 ml of absolute ethanol under reflux until dissolution is complete. This solution must be freshly prepared and should be filtered immediately before use.

MACRO PROCEDURE—

Extract the plant material or soil as described under "Experimental," p. 340, using the minimum amount of carbon tetrachloride. If the initial volume is appreciable, reduce it to about 10 ml by gentle distillation over a low flame, or by drawing a current of dry air over the surface of the liquid at about 35° C.

If acetone is used for the extraction of soil, evaporate to dryness by passing a current of dry air over the liquid at 35° C and dissolve the residue in 10 ml of carbon tetrachloride with warming, and then cool the solution.

Pass the solution through 5 g of aluminium oxide (previously wetted with carbon tetrachloride) supported on cotton-wool in a glass tube, 150 mm × 18 mm, having a constriction at the lower end. Wash through with five 5-ml portions of carbon tetrachloride. Gently distil the solvent from the eluate until the volume is about 10 ml and then evaporate to dryness at 35° C with a current of air.

When experience has shown it to be necessary, add 4 ml of acetic acid, warm to dissolve the residue, add 5 ml of potassium permanganate solution and place on a boiling-water bath for 10 minutes. Cool and decolorise by the addition, drop by drop, of sodium metabisulphite solution and then add 10 ml of water. Extract, successively, with vigorous shaking for 30 seconds each time, with 15, 5 and 5-ml portions of carbon tetrachloride. Combine the carbon tetrachloride extracts, add 10 ml of water and then 4 *N* potassium hydroxide, drop by drop, with shaking, until the aqueous layer is just alkaline to litmus paper. Run off the carbon tetrachloride layer, wash the aqueous layer with a little carbon tetrachloride, combine the carbon tetrachloride layers and wash with 5 ml of water. Run the carbon tetrachloride extract through anhydrous sodium sulphate and wash the water layer and desiccant with a little more solvent. Reduce the volume by gentle distillation to about 5 ml and evaporate to dryness at 35° C in a current of air. Continue with this residue, or with the residue obtained before addition of 4 ml of acetic acid if the permanganate oxidation procedure was unnecessary, as follows.

Add 2 ml of nitration acid and heat in a boiling-water bath for 10 minutes. Cool and slowly add 10 ml of water. Cool again and neutralise by the addition, with swirling and cooling, of 4 *N* potassium hydroxide until litmus paper just turns blue. Add 2 drops of 4 *N* potassium hydroxide in excess. Wash the cooled solution into a separating funnel with 5 ml of water. Rinse the flask with 15 ml of carbon tetrachloride, add the washings to the funnel and extract with vigorous shaking for 30 seconds. Re-extract with two further 5-ml portions of carbon tetrachloride, rinsing the flask. Combine the carbon tetrachloride extracts and wash them twice with 5-ml portions of water.

Run the carbon tetrachloride solution through anhydrous sodium sulphate and wash the separating funnel and desiccant with a little more solvent. Reduce the volume by distillation over a low flame to 5 ml and then evaporate to 0·5 ml at 35° C in a current of air.

Add 10 ml of 5 per cent. ethanolic potassium hydroxide solution, rotate for 15 seconds, and, after 5 minutes, measure the optical density spectrophotometrically in a 1-cm cell at a wavelength of 600 mμ when a Unicam SP600 spectrophotometer is used, or with an Ilford No. 607 filter when a Spekker absorptiometer is used.

MICRO PROCEDURE—

Extract the plant material or soil by hot percolation with acetone as described under "Experimental," p. 340, using the minimum amount of solvent. Evaporate to dryness at 35° C in a current of air.

Add 4 ml of acetic acid, warm to dissolve the residue, add 5 ml of potassium permanganate solution and heat on a boiling-water bath for 10 minutes. Cool and decolorise by the addition, drop by drop, of sodium metabisulphite solution. Extract, with vigorous shaking, with 10 and 5-ml portions of carbon tetrachloride. Run the carbon tetrachloride extracts through anhydrous sodium sulphate and evaporate the solvent to dryness at 35° C in a stream of air.

Add 1 ml of nitration acid and heat in a boiling-water bath for 10 minutes. Cool, add 5 ml of water and make just alkaline to litmus by adding 4 *N* potassium hydroxide solution.

Extract with vigorous shaking for 30 seconds with 10 ml of benzene. Wash the benzene layer with two 3-ml portions of water, run the benzene solution through anhydrous sodium sulphate into a 25-ml graduated stoppered cylinder, wash the desiccant and adjust the volume to 10 ml with benzene and add 5 ml of 5 per cent. ethanolic potassium hydroxide solution. Mix and after 5 minutes measure the optical density spectrophotometrically in a 2-cm cell.

Results

Calibration curves relating optical density to micrograms of *pp'*-DDT were prepared from the results of tests on *pp'*-DDT alone, of tetranitro-DDT prepared by the method of Backeberg and Marais,[11] of *pp'*-DDT taken through each method from the nitration stage and of *pp'*-DDT added to the solvent before the extraction of foliage, grain and soil. The degree of concordance was good, indicating no loss in the method and satisfactory recovery of DDT from the extracts of the materials examined.

In collaborative work with the Infestation Control Division of the Ministry of Agriculture, Fisheries and Food at Tolworth, carbon tetrachloride extracts of untreated grain to which known amounts of pure *pp'*-DDT and *gamma*-hexachloro*cyclo*hexane had been added, were prepared at Tolworth and sent to Long Ashton for analysis by the macro method. The results are shown in Table I.

Table I

Recovery of DDT from grain extracts by macro method

Sample	DDT added, p.p.m.	γ-Hexachloro*cyclo*hexane added, p.p.m.	DDT recovered, p.p.m.
A	0·5	Nil	0·5, 0·5
B.1	1·5	Nil	1·6, 1·7
B.2	1·5	0·5	1·5, 1·4
C.1	4·0	Nil	4·1, 3·9
C.2	4·0	2·0	4·0, 3·8
D.1	10·0	Nil	10·0, 9·9
D.2	10·0	4·0	10·0, 10·1
E	20·0	10·0	19·7, 19·9

The recovery by the macro method of DDT added to whole grain and from DDT-treated grain taken from storage is discussed later. The recoveries by the micro method of DDT added to acetone extracts of grain and soils are shown in Table II.

Table II

Recovery of DDT from grain and soil extracts by micro method

Sample	DDT added, p.p.m.	DDT recovered, p.p.m.
Grain	2·0	2·0
	4·0	3·9
	6·0	6·1
Sandy soil	1·5	1·4
	2·5	2·3
	3·5	3·1
	4·5	4·5
	5·5	5·5
Organic soil	1·5	1·6
	2·5	2·5
	3·5	3·2
	4·5	4·3
	5·5	5·9

For convenience, a standard disc for use with the macro method, which gives the colour intensities produced over the range 25 to 350 μg of DDT, has been prepared in collaboration with Tintometer Ltd. of Salisbury, Wilts., from whom it is available. The disc was designed only for analyses in which the permanganate treatment was not necessary. In the description of the method supplied by the firm, we now recommend the use of 5-g portions of alumina, with washing as described.

Discussion

Certain precautions and some experience in the use of the methods are necessary for satisfactory results. Chemicals of analytical-reagent quality should be used whenever possible and all-glass apparatus should be used throughout. Adequate separations and drainage should be allowed in all liquid - liquid extractions, and the amount of stopcock grease used should be kept to an absolute minimum. In the macro method, an opalescence on dilution of the nitration mixture with water indicates that more than 50 μg of DDT are present; if an appreciable amount of precipitate results, the carbon tetrachloride solution of the nitro compound should be diluted to a specific volume and an aliquot taken for the colour development. The test should be completed with the minimum of delay, particularly after extraction of the nitro compound with carbon tetrachloride. If crystals separate from the small volume of solvent before the addition of ethanolic potassium hydroxide, the test should be rejected.

The colour obtained in the examination of deposits on crops that had been subjected to weathering in the field was comparable with that obtained in the analysis of fresh deposits. This was probably due to the fact that any residual 4:4′-dichlorobenzophenone, which is formed from DDT under the influence of ultra-violet light and which gives a tangerine colour in the test, is removed by the alumina treatment. *op′*-DDT, which may be present in small amounts in spray deposits, gives a colour of lower intensity than that given by *pp′*-DDT and is unlikely to cause any significant error in the determination of the *pp′*-isomer. The presence of *gamma*-hexachloro*cyclo*hexane in grain does not cause interference in the determination of DDT.

Work has been carried out by B. S. J. Border and A. Taylor in the Infestation Control Division of the Ministry of Agriculture, Fisheries and Food on the recovery of DDT from grain by the macro method and we are indebted to Dr. E. E. Turtle for permission to refer to their results. Weighed amounts of DDT were added to 50-g portions of grain at concentrations over the range of 4 to 16 p.p.m. and the samples were analysed immediately. Recoveries of 88 to 110 per cent., with a mean value of 93 per cent., were found. These results are satisfactory in view of the difficulty of ensuring the even distribution of DDT crystals in the grain. Other samples, containing 8, 40 and 76 p.p.m. of added DDT, showed recoveries of 81 to 84 per cent. after storage for 5 weeks; on further extraction of the grain after grinding, the mean recovery of DDT was 88 per cent. The Infestation Control Division workers have also shown that extraction of the tetranitro-DDT with benzene followed by washing the extract with dilute alkali and the use of an aliquot without the removal of solvent in the colour formation gives results agreeing closely with those by the macro method, but with considerable saving of time.

It is desirable that a standard method based upon further collaborative work should be adopted for the determination of DDT in food commodities. Most of our work has been carried out on leaves and fruits from spraying trials, and for these materials the methods have proved to be satisfactory. Further work is required on the recovery of DDT from grain after storage and on the details of the method of analysis to be used. It may be that a combination of the principles of the macro and micro methods, as suggested by the Tolworth workers, would be most acceptable. Fatty materials, such as groundnuts and oil-cake, need special consideration.

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A Method for the Detection of Traces of Acrylonitrile

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A chromatographic method is described for the detection and approximate determination of traces of acrylonitrile. The method is based on a reaction between acrylonitrile, thiourea and hydrochloric acid to yield 2-(2-cyanoethyl)*iso*thiuronium chloride, which is detected by paper chromatography with an ammoniacal silver nitrate spray reagent. The method is widely applicable, specific and highly sensitive; it makes possible the detection of acrylonitrile in amounts of the order of 1 μg.

In the last 10 years, acrylonitrile has achieved many technological applications, *e.g.*, as the raw material for artificial fibres and synthetic rubber, for various organic synthetic products and also as a fumigant insecticide for crops. The need for a suitable method for its detection has consequently extended into various industries. As acrylonitrile is a highly toxic substance, a specific and sensitive method is required for its qualitative detection as well as for the determination of residual amounts of it in industrial raw materials and products, air, industrial waste waters, crops, food-stuffs and also in various physiological systems, in order to follow its metabolism, *e.g.*, urine, blood and blood serum.

Of the numerous chemical reactions of acrylonitrile only three have been suggested for its qualitative detection. The first of these makes use of its reaction with piperidine to form β-piperidinopropionitrile,[1] the picrate of which melts at 161° to 162° C; this reaction can be used to detect concentrations of acrylonitrile as low as 1 per cent. The second method, a colorimetric test for amides and nitriles, is based on the reaction of acrylonitrile with hydroxyammonium chloride in propylene glycol. In the presence of potassium hydroxide, after being heated and subsequently cooled, a red to violet colour is formed with ferric chloride.[2] Finally, a method was suggested for the detection of hydrogen cyanide or acrylonitrile in air or other gases, based on contact with a reagent consisting of *o*-tolidine and cupric sulphate in glycerol on silica gel. The presence of hydrogen cyanide or acrylonitrile causes a colour change to blue or blue-green.[3] The first of these reactions is not sufficiently sensitive and the others are not specific.

Established quantitative chemical methods for the determination of acrylonitrile are based either on titration of the ammonia liberated when acrylonitrile is hydrolysed with concentrated alkali[4] or sodium and ethanol[5] or else on the oxidation of acrylonitrile with potassium permanganate[6,7,8] or a mixture of chromic and sulphuric acids.[9] None of these methods is sufficiently specific for the reliable detection of residual traces of acrylonitrile. Beesing, Tyler, Kurtz and Harrison[10] have suggested a method based on the cyanoethylation of dodecyl mercaptan in the presence of potassium hydroxide as catalyst. The reaction is carried out in *iso*propyl alcohol[11] and the excess of mercaptan is titrated in an acidified medium with potassium bromate and potassium iodide. If the solution is coloured, the silver salt of the mercaptan can be precipitated and then determined potentiometrically.[12] The cyanoethylation reaction between acrylonitrile and dodecyl mercaptan has also been applied to the determination of concentrations of acrylonitrile in air up to 150 mg per cubic metre.[13] The ability of acrylonitrile to cyanoethylate *iso*propyl alcohol and the mercaptan simultaneously in an alkaline medium has been used in a modified method for the simultaneous determination of acrylonitrile and 1-cyano-1:3-butadiene.[14] A similar quantitative method is based on the reaction between acrylonitrile and sodium or potassium glycocholate.[15] For the determination of acrylonitrile, several quantitative methods have recently been suggested. One of these is based on a general reaction of $\alpha\beta$-unsaturated compounds, *viz.*, the addition of sodium hydrogen sulphite to acrylonitrile to form a substituted sodium sulphonate; the optimum pH for this reaction is attained by the addition of a measured excess of *N* sulphuric acid.[16] Another method involves the reaction of acrylonitrile (and of $\alpha\beta$-unsaturated compounds in general) with morpholine in the presence of acetic acid to form a tertiary amine, which can be titrated with methanolic hydrochloric acid after the excess of morpholine has been converted to the neutral amide with acetic anhydride.[17] Other methods are based on

the addition of sodium sulphite to acrylonitrile and subsequent titration of the sodium hydroxide liberated[18]; and also on the addition of sodium hydrogen sulphite, the excess of which is titrated with an alkali solution.[19]

Physical methods can also be used for the detection and determination of acrylonitrile; spectrophotometric,[20] infra-red absorption[21,22,23] and polarographic procedures[24 to 29] have been reported.

Principle of the method

It has been reported in a review of the chemical properties of acrylonitrile[11] that it reacts with thiourea, in the presence of a basic catalyst, to form 2-(2-cyanoethyl)*pseudo*-thiourea,[30,31] according to the equation—

$$H_2N{\cdot}CS{\cdot}NH_2 + CH_2 = CH{\cdot}CN \xrightarrow{OH^-} NH = \overset{\displaystyle NH_2}{\overset{|}{C}}{-}S{-}CH_2{\cdot}CH_2{\cdot}CN.$$

According to another report, however, thiourea and acrylonitrile do not react at 100° C in the presence of alkali.[31,32]

In the course of our study of acrylonitrile,[33] we found that a similar cyanoethylation reaction occurs between acrylonitrile and thiourea in the presence of halogen acids in an aqueous or alcoholic medium. The halogen acid takes part in the reaction, the main product of which is the corresponding *iso*thiuronium salt, according to the equation—

$$CN{\cdot}CH = CH_2 + H_2N{\cdot}CS{\cdot}NH_2 + HX \longrightarrow \left[CN{\cdot}CH_2{\cdot}CH_2{-}S{-}C(=NH)(H)(NH_2) \right]^+ X^-,$$

where X represents Cl, Br or I.

The addition product of acrylonitrile and hydrochloric acid, β-chloropropionitrile, reacts in the same way and forms 2-(2-cyanoethyl)*iso*thiuronium chloride directly with thiourea.[34] It is hoped that details of the probable intermediate formation of β-chloropropionitrile from acrylonitrile and aqueous or alcoholic hydrochloric acid will be dealt with in a separate paper. The homologous methacrylonitrile, when allowed to react with thiourea under the same conditions, does not form a corresponding *iso*thiuronium salt.

In the presence of concentrated hydrochloric acid the reaction occurs with quantitative consumption of acrylonitrile. The resulting 2-(2-cyanoethyl)*iso*thiuronium chloride can be detected by paper chromatography with an ammoniacal silver nitrate spray reagent. This method is both specific and simple; it permits the detection of amounts of acrylonitrile as small as 1 μg. The corresponding bromide (m.p. 177° C) and iodide (m.p. 131° to 132° C) can also be detected by paper chromatography, as they have different R_F values, but the procedure is less sensitive and considerable complications can arise, particularly with the iodide.

Experimental

To verify the conditions of the reaction between acrylonitrile, thiourea and hydrochloric acid, the optimum ratio of reactants was first studied. It was found that the reaction occurred almost stoicheiometrically when an excess of hydrochloric acid was present. In order to increase the sensitivity of detection of minute amounts of acrylonitrile, *e.g.*, from 1 to 5 μg, it was necessary to increase proportionately the amounts of thiourea and hydrochloric acid in the reaction solution, up to 35 moles and 50 moles, respectively, per mole of acrylonitrile. Either water or a polar organic solvent can be used as the reaction medium. Ethanol, *n*-propyl alcohol and *iso*propyl alcohol proved to be the most suitable solvents; *iso*butyl alcohol, *tert.*-butyl alcohol and acetone caused the formation of interfering by-products, especially at the lower concentration of acrylonitrile. The reaction takes place at ordinary temperatures, but can be accelerated by heating, *e.g.*, under reflux. When different amounts of acrylonitrile are allowed to react with thiourea in the absence of hydrochloric acid, or in an alkaline medium, the *iso*thiuronium salt cannot be detected; this is in accordance with the findings of Hurd and Gershbein.[32]

It was also found that, after the completion of the reaction, the solution can be diluted with water or an organic polar solvent or, alternatively, concentrated to a certain extent by evaporation, without any apparent effect on the detection of acrylonitrile. Dilution can

be practically unlimited, but evaporation, which can only be carried out with alcoholic solutions, must not be continued after an approximate concentration of 0·1 mg of acrylonitrile per 2 ml of solution has been reached. The chromatographic spots in this instance, however, are less marked, being about half their normal intensity. It is preferable, therefore, to concentrate the test solution by distilling the acrylonitrile from the original sample, either in a current of pre-heated air or azeotropically with *iso*propyl alcohol.

By using this procedure, it is possible to determine minute amounts of acrylonitrile, when working with specified volumes, down to a minimum of 1 μg. The colour intensity of the *iso*thiuronium spot produced by 1 μg of acrylonitrile corresponds to that produced by 0·3 to 0·5 μg of standard *iso*thiuronium chloride solution.

Impurities in commercial acrylonitrile do not affect its detection or determination.

Method

Reagents—

All reagents should be of recognised analytical grade.

Hydrochloric acid, concentrated.

Ammonia solution, 10 per cent. aqueous.

Sodium thiosulphate solution, 2 per cent.—A 2 per cent. aqueous solution of sodium thiosulphate, $Na_2S_2O_3.5H_2O$.

Thiourea.

Ethanol or iso*propyl alcohol.*

n-*Butyl alcohol*—Saturate with distilled water before use.

Ammoniacal silver nitrate solution (Tollens's reagent)—Prepare by treating a 0·1 *N* aqueous solution of silver nitrate with an equimolecular amount of 5 per cent. aqueous sodium hydroxide. Add 5 *N* aqueous ammonia to the precipitated silver oxide, with constant agitation, until the solid just dissolves, and then make the solution slightly ammoniacal by the further addition of aqueous ammonia. This reagent must be freshly prepared before use.

2-(2-*Cyanoethyl*)iso*thiuronium chloride, ethanolic standard solution*—Dissolve 2 g of the *iso*thiuronium salt, prepared by the procedure described on p. 348, in 1 litre of ethanol.

Preparation of the sample for chromatography—

By absorption, distillation or extraction from the system containing acrylonitrile, prepare in ethanol or *iso*propyl alcohol a solution containing 5 to 10 mg of acrylonitrile per 10 ml. Place 10 ml of this solution in a 50-ml flask, add 0·5 g of thiourea and then 0·75 ml of concentrated hydrochloric acid. Boil the reaction mixture under reflux on a water bath for 30 minutes. When cool, use this solution for the paper-chromatographic procedure.

When the acrylonitrile is present in the form of an aqueous solution, follow the same procedure, but heat under reflux at a correspondingly higher temperature.

When 10 ml of the alcoholic solution contain less than 5 mg of acrylonitrile, follow the same procedure, but make correspondingly smaller additions of thiourea and hydrochloric acid, *e.g.*, 5 and 10 times diminished at acrylonitrile contents of 2 and 1 mg per 10 ml of solution, respectively. After 15 to 30 minutes' boiling under reflux, evaporate the reaction solution on a water bath to a specified volume, not less than 2 ml, and use this for the chromatographic procedure. If the original solution contains more than 10 mg of acrylonitrile per 10 ml, dilute it with the solvent until the *iso*thiuronium spot that corresponds to the minimum amount of 1 μg of acrylonitrile is achieved by paper chromatography. In this instance, it is not necessary to alter the additions of thiourea and hydrochloric acid. It is always preferable to estimate the amount of acrylonitrile present in the sample by a preliminary experiment, in order to establish the precise conditions for the final procedure.

Procedure for developing the chromatogram—

On a strip of Whatman No. 4 filter-paper, 150 mm × 300 mm, place, by means of a micropipette, at least 0·001 ml of the reaction solution along a line 8 cm from the upper edge of the strip. Allow the solvent to evaporate and then repeat the procedure several times, making any number of additions up to ten and allowing the solvent to evaporate after each addition. Chromatograms are thus prepared from 0·001 to 0·01 ml of the reaction solution, and these can be used to achieve an approximate evaluation of the amount of acrylonitrile present.

To compare the position and character of the *iso*thiuronium spots detected with that of a standard solution, apply simultaneously 0·001 ml of the latter by means of a micropipette.

Suspend the strip of filter-paper in a chromatographic tank for 2 hours to attain equilibrium with the atmosphere of *n*-butyl alcohol and water vapours. Dip the upper end of the paper strip in *n*-butyl alcohol that has been saturated with water and allow the solvent front to travel 25 to 28 cm down the paper over a period of about 4 hours.

Remove the strip from the tank, mark the position of the solvent front and then allow the paper to dry at room temperature until all the solvent has evaporated (12 to 24 hours).

PROCEDURE FOR COLOUR DEVELOPMENT—

Spray the dry strip with Tollens's ammoniacal silver nitrate reagent. The dark brown spot of thiourea, which is the most substantial one on the chromatogram, R_F 0·43, appears immediately, owing to the presence of a considerable excess of this substance. As spraying proceeds, a typical yellow spot of 2-(2-cyanoethyl)*iso*thiuronium chloride appears, R_F about 0·25, depending on the concentration of acrylonitrile present. This spot soon darkens until it is dark grey, with a yellow centre at higher concentrations of acrylonitrile. The development of the spot, particularly at minute concentrations of acrylonitrile, can be accelerated by heating for 5 minutes at 100° C and subsequently washing the chromatogram with a 10 per cent. aqueous solution of ammonia and then with distilled water. A faint brownish spot, R_F 0·32, which gradually darkens, also appears; this spot corresponds to the reaction of thiourea and hydrochloric acid with the alcohol and appears even in the absence of acrylonitrile. When the standard *iso*thiuronium chloride solution is used, only the spot R_F 0·25 appears.

The spots of *iso*thiuronium chloride have a tendency to "tail" somewhat as the concentration of acrylonitrile increases from 1 μg up to approximately 10 μg per 10 ml, but the position of the solvent front remains constant. The position, character and colour of these spots correspond closely to those obtained from standard solutions at the respective concentrations.

When the colours of the spots have developed to maximum intensity, wash the chromatogram thoroughly with distilled water and allow it to dry at room temperature. The removal of the excess of ammoniacal silver nitrate solution and the fixation of the chromatogram are finally accomplished by washing with a 2 per cent. solution of sodium thiosulphate and water.

The presence of any proportion of methacrylonitrile does not interfere with the detection of acrylonitrile. When the chromatogram is treated with ammonia solution after it has been sprayed with ammoniacal silver nitrate solution, methacrylonitrile slowly forms a faint yellowish to brownish spot just above that of thiourea, thus producing an apparent "tailing" of the thiourea spot.

To determine approximately the acrylonitrile content of the solution, record the *iso*thiuronium spot at which a faint durable grey colour just appears. This spot corresponds to 1 μg of acrylonitrile. From the concentration of the solution examined and the amount of it necessary to produce that spot, calculate the approximate amount of acrylonitrile present in 1 kg of the original sample.

PREPARATION OF 2-(2-CYANOETHYL)*iso*THIURONIUM CHLORIDE

REAGENTS—

Acrylonitrile—Technical grade.
Thiourea—Analytical-reagent grade.
Hydrochloric acid, concentrated—Analytical-reagent grade.
iso*Propyl alcohol*—Technical grade.
Ethanol—Technical grade.

PROCEDURE—

Dissolve 25 g of acrylonitrile in 200 ml of *iso*propyl alcohol contained in a 500-ml flask. Add 65 ml of concentrated hydrochloric acid and 40 g of thiourea. Boil the reaction mixture under reflux on a water bath for 30 minutes. After it has been cooled and shaken thoroughly, the solution deposits fine needles of 2-(2-cyanoethyl)*iso*thiuronium chloride, which are separated and dried in air. By part evaporation and crystallisation of the mother-liquor, further portions of *iso*thiuronium chloride can be obtained. Purify the product by recrystallisation from ethanol until it melts between 165·5° and 166° C. This method of preparation gives an approximately 60 per cent. yield of the pure product.

Purity test—The purity of the 2-(2-cyanoethyl)*iso*thiuronium chloride can be tested by subjecting the material to the above-described paper-chromatographic procedure. Only one spot, R_F 0·25, should be produced.

Application of the method

The proposed method can be applied for the detection and approximate determination of trace amounts of acrylonitrile in a wide range of materials, such as industrial products, food-stuffs, crops, air and waste waters, and in physiological systems such as urine, blood and blood serum. It is hoped that the respective analytical procedures, together with any interfering effects that arise from the character of the material being examined—crops, urine, blood and so on—will be dealt with in separate publications.

The proposed method may find valuable application in food technology by specifying the amount of material under examination that should not produce a coloured *iso*thiuronium chloride spot by the method, and so be in accordance with the official tolerances for acrylonitrile in the material.

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Determination of Traces of Manganese with Leucomalachite Green

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A sensitive absorptiometric method for determining traces of manganese, leucomalachite green being used as reagent, has been developed. Manganous ions are oxidised to permanganic acid at room temperature by potassium periodate in a sodium acetate - acetic acid buffer solution, and a solution of leucomalachite green is added; this reagent is oxidised by permanganic acid to form a blue-green colour, which is measured at about 620 mμ. The effects of various conditions and of 36 foreign ions are examined. When applied to plant materials, the recommended procedure gives results in good agreement with the absorptiometric permanganate method, and with a precision of approximately ±5 per cent.

For many years the absorptiometric measurement of permanganate ions[1] has been applied to the determination of manganese in plant materials and soil extracts. The method is simple and relatively free from interference, but, for small sample weights or very low manganese contents, it is often not sufficiently sensitive. An extremely sensitive test for detecting traces of manganese, using *pp'*-tetramethyldiaminodiphenylmethane (tetrabase or methane base) as reagent, has been widely used.[2,3,4,5] Harry[6,7] first described a quantitative determination with this reagent, ammonium persulphate being used as the oxidant. More recently, Nicholas and Fisher,[8,9] who used potassium periodate as oxidant, measured the blue colour formed initially with tetrabase. This colour, however, is too fugitive for satisfactory measurement; further, at the low temperature (below 10° C) specified, mist forms on the walls of the optical cell and causes errors in absorptiometry. Cornfield and Pollard[10] made use of the green colour that forms 10 minutes after the addition of the reagents, but, both in the presence of manganese and in blank tests, this colour continues to change, and, although it is less transient than the initial blue colour, it cannot be accurately measured.

The use of a related compound, *pp'*-tetramethyldiaminotriphenylmethane, also known as leucomalachite green, for determining traces of manganese was reported by Schwarz, Fischer and Hagemann[11] and by Gates and Ellis.[12] Schwarz, Fischer and Hagemann developed the colour in a lactic acid solution. Gates and Ellis used potassium periodate in a mixture of nitric and phosphoric acids at 100° C to oxidise manganous ions, and then produced a yellow colour with leucomalachite green at 80° C. I found that the latter procedure gave excessive blank values and that the effects of variations in temperature or time were too critical to permit adequate reproducibility. It was found, however, that leucomalachite green produced a blue-green colour with traces of permanganate at room temperature in a sodium acetate - acetic acid buffer solution, and this appeared to be suitable for the quantitative determination of manganese. Under suitable conditions the blank value was negligible and the colour intensity was constant. An investigation into the various factors influencing colour formation and the effects of various foreign ions resulted in the development of a satisfactory method for traces of manganese, which gives good agreement with the absorptiometric permanganate method and is about 200 times more sensitive.

Experimental

Absorption characteristics of the colour—

In preliminary experiments, the colour formed by oxidising leucomalachite green with manganous ions and potassium periodate was found to be similar to that formed by direct oxidation with an equivalent amount of potassium permanganate, and also to that of malachite green. Ferric or iodide ions in the presence of periodic acid also produced a similar, but much less intense colour. The identity of the various colours was confirmed by comparing absorption spectra measured at from 400 to 700 mμ with a Unicam SP350 spectrophotometer. In each instance a maximum absorption at about 620 mμ and a lesser peak at about 420 mμ were found. The reactions were carried out at 19° C, at pH 3·35 obtained with a sodium acetate - acetic acid buffer solution.

Potassium periodate alone did not produce a colour at this temperature, but, when heated to 100° C, a colour developed that had a maximum absorption at 590 mμ. It was evident that the colour formed in the presence of manganese is due to permanganic acid and not directly to the periodic acid.

The absorption spectrum showed that a red filter (Chance OR2) is suitable for measurement of the colour.

CONDITIONS REQUIRED FOR THE DETERMINATION—

It was found that factors influencing colour formation included acidity, amounts of potassium periodate and leucomalachite green present, temperature and the times allowed for preliminary oxidation of manganese and for colour development. These all need to be standardised; the optimum conditions were established as follows.

Effect of acidity—A satisfactory colour was produced only in a narrow pH range, namely from 3 to 4. Below pH 3, the development of colour was slow and incomplete, and above pH 4 leucomalachite green was precipitated. A buffer solution was therefore necessary to keep the pH within this range. Sodium acetate - acetic acid and sodium borate - acetic acid buffer solutions were found to be equally suitable. The effects of variations in pH within the range of 3 to 4 and of two different concentrations of sodium acetate, 0·25 and 0·5 g of the hydrated salt per 50 ml, were investigated. The colours formed by 0, 0·4 and 0·8 μg of manganese, as manganous sulphate, were developed in 50-ml calibrated flasks by adding the required amounts of sodium acetate and acetic acid, 3 ml of 0·2 per cent. potassium periodate solution and 0·5 ml of a 0·1 per cent. solution of leucomalachite green in 0·1 *N* hydrochloric acid. The solutions were diluted to 50 ml and their optical densities measured 1 hour later in 2-cm cells with a Hilger Biochem absorptiometer, a Chance OR2 red filter being used. The results are shown in Fig. 1.

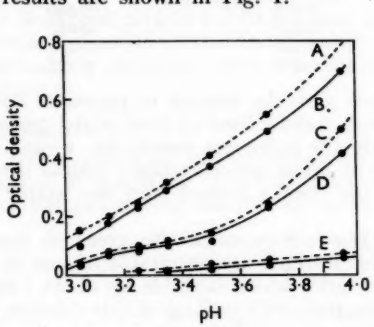

Fig. 1. Effect of acidity: curve A, 0·4 μg of manganese with 0·25 g of sodium acetate added; curve B, 0·4 μg of manganese with 0·5 g of sodium acetate added; curve C, 0·2 μg of manganese with 0·25 g of sodium acetate added; curve D, 0·2 μg of manganese with 0·5 g of sodium acetate added; curve E, no manganese with 0·25 g of sodium acetate added; curve F, no manganese with 0·5 g of sodium acetate added

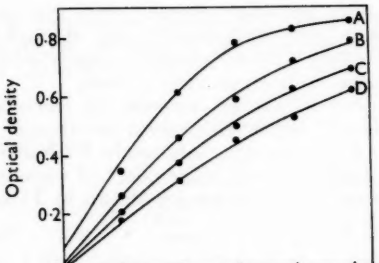

Fig. 2. Effect of pH on calibration curve: curve A, pH 3·55; curve B, pH 3·35; curve C, pH 3·25; curve D, pH 3·10

The sensitivity decreased rapidly as the acidity increased. An intense colour appeared rapidly at pH 4, but an appreciable blank value was found at pH 3·5 and above. The higher concentration of sodium acetate had a suppressing effect, so 0·25 g was used in all subsequent work.

The effect of acidity was further examined at four different pH values. Buffer solutions were prepared by dissolving 50 g of sodium acetate and 200, 300, 400 and 500 ml of glacial acetic acid in water and diluting the solutions to 1 litre to give pH values of 3·55, 3·35, 3·25 and 3·10, respectively. Solutions containing from 0 to 1 μg of manganese were treated by adding 5 ml of buffer solution, 5 ml of 0·2 per cent. potassium periodate solution and 1 ml of 0·1 per cent. leucomalachite green solution, and then diluting to 50 ml. The absorptiometer readings are shown in Fig. 2.

The optical densities increased as the acidity decreased; at pH 3·55 the sensitivity was about twice that at pH 3·10. None of the four curves is linear, but those at lower pH values are more nearly so. A sodium acetate - acetic acid buffer solution at pH 3·25, which gives a final pH of 3·35, was selected, as it gives a reasonably low blank value with adequate sensitivity.

In these conditions, the further addition of acid equivalent to 0·25 ml of 0·1 *N* hydrochloric acid had no appreciable effect on the optical density, but increased amounts proportionately reduced it. Hence, the amount of excess acid contained in extracts of plant ash should be the minimum required for complete dissolution.

Effect of various amounts of potassium periodate—At first, saturated potassium periodate solution was used. It was soon found that the concentration of periodate in the saturated solution varied with temperature and length of storage. A 0·2 per cent. solution was therefore prepared instead. This reagent is stable for about 5 days. The effect of various amounts of periodate on the colour intensity was examined by adding from 1 to 10 ml of 0·2 per cent. periodate solution per test. The optical densities for 0, 0·4 and 0·8 μg of manganese are shown in Table I.

TABLE I

EFFECT OF VARIOUS AMOUNTS OF 0·2 PER CENT. POTASSIUM PERIODATE SOLUTION

Amount of 0·2 per cent. potassium periodate solution added, ml	Absorptiometer reading in absence of manganese	Absorptiometer reading in presence of 0·4 μg of manganese	Absorptiometer reading in presence of 0·8 μg of manganese
1·0	0·006	0·088	0·170
2·0	0·012	0·178	0·320
3·0	0·014	0·270	0·492
4·0	0·020	0·332	0·560
5·0	0·030	0·390	0·640
7·0	0·038	0·450	0·700
10·0	0·044	0·486	0·720

The optical density due to manganese increased with the amount of periodate added; so did that of the blank solution. The amount was standardised at 5 ml of 0·2 per cent. potassium periodate solution, since this gave nearly the maximum sensitivity, while larger amounts gave increasingly wide deviations from a linear concentration - optical density relationship. When smaller amounts were used, the colours formed were less stable and continued to increase after 1 hour.

Effect of various amounts of leucomalachite green—Leucomalachite green is readily soluble in acetone, chloroform or ethanol, but these solvents are unsuitable for use in the test. A 0·1 per cent. solution in 0·1 *N* hydrochloric acid, which is stable for about 1 week, was finally adopted. The effect of various amounts from 0·25 to 3 ml of this solution was examined. The results are shown in Table II.

TABLE II

EFFECT OF VARIOUS AMOUNTS OF 0·1 PER CENT. LEUCOMALACHITE GREEN SOLUTION

Amount of 0·1 per cent. leucomalachite green solution added, ml	Absorptiometer reading in absence of manganese	Absorptiometer reading in presence of 0·4 μg of manganese	Absorptiometer reading in presence of 0·8 μg of manganese
0·25	0·012	0·288	0·488
0·50	0·014	0·350	0·574
1·0	0·018	0·366	0·630
2·0	0·016	0·340	0·553
3·0	0·012	0·230	0·460

Since the optical density increased as the volume of 0·1 per cent. leucomalachite green solution was increased up to 1 ml and larger amounts reduced the intensity (probably because of the hydrochloric acid contained in the reagent), the addition of 1 ml per test was adopted.

Effect of temperature—Both the colour intensity due to manganese and that of the blank solution increased somewhat with temperature up to 25° C, and above 30° C the results were erratic. A temperature of 25° C was therefore adopted as standard.

Effect of variation in the times of reaction—The effects of variation in the times allowed for oxidation of manganous ions to permanganate and for the reaction of this with leucomalachite green were examined. One hour was allowed for the second reaction when the

time for the first was varied; when the time for the second reaction was varied, 20 minutes were allowed for the first. The results are shown in Fig. 3.

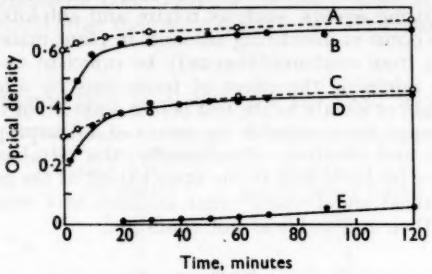

Fig. 3. Effect of time. Time of standing before adding leucomalachite green: curve A, 0·8 μg of manganese; curve C, 0·4 μg of manganese. Time of standing after adding leucomalachite green: curve B, 0·8 μg of manganese; curve D, 0·4 μg of manganese; curve E, no manganese

When a longer time was allowed for the preliminary oxidation, the colour subsequently developed was more intense and more consistent. It appears that a 30-minute standing period before the addition of leucomalachite green is sufficient to complete the preliminary oxidation of up to 1 μg of manganese. After leucomalachite green had been added, the colour developed rapidly for 30 minutes, and then more slowly. Standing for 1 hour gave maximum stable coloration without unduly increasing the blank value. Periods of 30 minutes for preliminary oxidation and 1 hour for colour development were adopted as the standard procedure.

INTERFERENCE—

In this investigation various cations were added in the form of chloride, sulphate or nitrate, and anions as potassium or sodium salts. The maximum amounts of 36 ions that could be present without causing interference are shown in Table III.

TABLE III

EFFECT OF FOREIGN IONS

Ion	Maximum amount that does not cause interference, mg	Effect on colour intensity of excess of ion	Ion	Maximum amount that does not cause interference, mg	Effect on colour intensity of excess of ion
Aluminium ..	0·1	Increase	Chloride ..	15	Decrease
Ammonium ..	5	Decrease	Chromate ..	0·05	Increase
Calcium	10	Decrease	Citrate	0·1	Decrease
Cobalt	0·1	Increase	Cyanide	0·2	Increase
Copper	0·2	Decrease	Dichromate ..	0·05	Increase
Ferric iron ..	0·002	Increase	Fluoride ..	0·5	Decrease
Ferrous iron ..	0·01	Decrease	Iodate	2	Decrease
Lead	0·1	Decrease	Iodide	0·001	Increase
Magnesium ..	8	Decrease	Molybdate ..	0·5	Increase
Nickel	0·1	Increase	Nitrate	2	Increase
Potassium ..	10	Decrease	Nitrite	0·002	Decrease
Sodium	12	Decrease	Orthophosphate	10	Decrease
Zinc	0·3	Decrease	Oxalate ..	0·05	Increase
Acetate ..	15	Decrease	Perchlorate ..	8	Increase
Arsenate ..	1	Increase	Silicate	1·5	Increase
Bicarbonate ..	5	Increase	Sulphate ..	12	Decrease
Borate	10	Increase	Sulphite ..	0·01	Decrease
Bromide ..	0·5	Increase	Thiosulphate ..	0·01	Increase

Among the cations, calcium, magnesium, potassium and sodium in fairly large amounts had no effect. Both ferric and ferrous ions seriously interfered; as little as 2 μg of ferric

ion caused a significant error. Other metals, such as cobalt, copper, lead, nickel and zinc, affected the test only when present in amounts greater than 100 times the manganese content.

Among the anions, chromate, dichromate, iodide, oxalate and thiosulphate increased the optical density; reducing agents, such as nitrite and sulphite, decreased it.

Iodide is unlikely to occur in interfering amounts in plant material, but the iron present in some plants or arising from contamination may be sufficient to interfere with the determination. Attempts to minimise the effect of ferric ions by adding a small amount of phosphate, fluoride, oxalate or citrate to the test before addition of the reagents were without success. Removal of iron as ferric chloride by means of a di*iso*propyl ether extraction[13] was found to be both simple and effective. Incidentally, the tetrabase method was found to be sensitive to interference by ferric iron to the same extent as the proposed method, and the statement made by Cornfield and Pollard[10] that addition of a small amount of phosphate minimised the effect in their method was not confirmed.

Method

Reagents—

Buffer solution—Dissolve 50 g of analytical-reagent grade hydrated sodium acetate in water containing 400 ml of analytical-reagent grade glacial acetic acid and dilute to 1 litre.

Potassium periodate solution, 0·2 per cent.—Dissolve the required amount of analytical-reagent grade potassium periodate in water, with heating to 80° C and stirring.

Leucomalachite green solution, 0·1 per cent.—Dissolve 0·1 g of leucomalachite green (*pp'*-tetramethyldiaminotriphenylmethane) in water containing 1 ml of concentrated hydrochloric acid at 80° C. Cool the solution and dilute it to 100 ml. The leucomalachite green obtained from Hopkin & Williams Ltd. (slightly brownish colour) was found to be suitable for this method; the solution is slightly pink. A solution prepared from a supply of the product of the British Drug Houses Ltd. (pale green) was green in colour and gave a high blank value.

Standard manganese stock solution—Dissolve 0·203 g of analytical-reagent grade manganous sulphate, $MnSO_4.4H_2O$, in water containing 2 ml of concentrated sulphuric acid and dilute to 1 litre. This solution contains 50 p.p.m. of manganese.

Standard manganese working solution—Dilute 2 ml of stock solution to 1 litre with water. This solution contains 0·1 μg of manganese per ml.

Preparation of the extract—

Weigh 0·1 g of plant material into a small silica basin and ignite in a muffle furnace at 550° C. Cool the basin and add a few millilitres of water and 1 ml of concentrated hydrochloric acid. Evaporate to dryness on a sand-bath and ignite the residue over a small flame. Add 3 ml of approximately 7 *N* hydrochloric acid to the ash and stir with a thin glass rod until iron oxides have dissolved, warming the mixture if necessary. Transfer the solution to a small separating funnel and rinse the basin with 2 ml of 7 *N* hydrochloric acid. Add 5 ml of di*iso*propyl ether and shake for about 1 minute. When the layers have separated, run the hydrochloric acid layer into the original basin and evaporate to dryness on a sand-bath. To the residue, add 15 ml of water acidified with 0·5 ml of approximately 0·1 *N* hydrochloric acid, heat to the boiling-point, and then filter through a Whatman No. 40 filter-paper into a 100-ml calibrated flask. When cool, dilute to the mark with water.

Procedure—

By pipette, place an aliquot of the extract containing up to 1 μg of manganese in a 50-ml calibrated flask and dilute it to 35 ml with water. Add 5 ml of buffer solution and 5 ml of 0·2 per cent. potassium periodate solution with shaking. Place the flask in a thermostatically controlled water bath at 25° C for 30 minutes and then add 1 ml of 0·1 per cent. leucomalachite green solution. Dilute to the mark, mix well and replace the flask in the water bath. One hour after mixing, measure the optical density against water absorptiometrically in a 2-cm cell, using a red (Chance OR2) filter. At the same time carry out a blank experiment and prepare a calibration curve for 0 to 1 μg of manganese by treating aliquots from 0 to 10 ml of the standard working solution by the same procedure.

From this curve, read the manganese concentration of the sample solution and express the result as p.p.m. in dry matter.

Accuracy of the proposed method

The manganese contents of 17 plant materials were determined by both the proposed method and the absorptiometric permanganate method. With the former, determinations with and without di*iso*propyl ether treatment were made. The results are shown in Table IV.

Table IV

Determination of manganese in plant material

Sample	Manganese found by the permanganate method, p.p.m. in dry matter	Manganese found by the proposed method— in presence of iron, p.p.m. in dry matter	Manganese found by the proposed method— in absence of iron, p.p.m. in dry matter
Potato leaf	76	85	75
Potato leaf	266	260	254
Potato tuber	6	9	6
Mustard	16	27	18
Fodder beet leaf	14	22	16
Clover leaf	54	60	58
Pea leaf	16	15	16
Pea leaf	67	69	70
Lucerne	21	28	30
French bean leaf	177	170	165
Broad bean leaf	115	125	117
Buckwheat	38	52	40
Oat grain	22	24	23
Oat straw	17	17	19
Grass	73	72	77
Barley	12	13	14
Wheat	172	185	165

There was satisfactory agreement between the two methods over a wide range of plants. The removal of iron did not always give a closer agreement.

On the basis of duplicate determinations in the course of routine analysis of a number of samples of plant material by the proposed method, a precision of about ± 5 per cent. is indicated.

Discussion

The mechanism of the formation of malachite green by oxidation of the leuco-compound is uncertain, but it is probably similar for a number of oxidising agents of high potential, including permanganate.[14] In the present work, ferric and iodide ions in the presence of periodate were found to produce the reaction; it has also been used to determine gold[15] and to detect peroxide.[16] The reaction is therefore not specific for manganese; however, only iron need be considered as a likely source of interference in plant materials and this is readily removed by extraction with di*iso*propyl ether.

The sensitivity of the proposed method is similar to that of the tetrabase methods,[9,10] and about 200 times greater than that obtained by absorptiometric measurement of the permanganate ion. Its advantage over the latter is its applicability to small sample weights or to materials that have very low manganese contents. It is superior to tetrabase methods in the formation of a stable colour, giving low blank values and a satisfactory calibration curve for the range 0 to 1 μg.

The colour is readily extracted with chloroform, if necessary with a much smaller volume, thereby increasing the sensitivity attainable.

In addition to plant material, ammonium acetate extracts of a number of soil samples have been satisfactorily analysed by the proposed method. It seems likely that it could be usefully applied to water analysis.

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Inorganic Chromatography on Cellulose

Part XVII.* The Separation of the Non-volatile Platinum Metals

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Rapid and simple methods are described for the separation of macro amounts of platinum, palladium, iridium and rhodium. Quantitative separations of widely different amounts of these metals are made possible by the use of cellulose powder as adsorbent and an acidified ketone as solvent, and by control of the valency level of the complex chlorides. The separations are based on the widely different mobilities of the complex chlorides of the four non-volatile platinum metals in a suitable solvent system and in contact with the cellulose powder.

The work described in this paper is an extension to the macro scale of earlier work[1] on the chromatographic separation of microgram amounts of the platinum metals. With mixtures of platinum metals, an upper limit of 100 mg of any one metal has been only rarely exceeded, although this does not imply that larger amounts cannot be separated under the correct conditions.

The chromatographic separations take place on a column of cellulose supported in a glass tube of internal diameter $1{\cdot}8 \pm 0{\cdot}1$ cm, the column height being adjusted, within limits, to the amounts of the metals present and to the separation being attempted. By using a suitable solvent mixture for elution, the platinum metal chloride complexes display widely different mobilities on cellulose columns. The oxidising or reducing nature of the experimental conditions is of importance when the separations involve iridium. If oxidising conditions are maintained throughout, iridium is rapidly eluted together with platinum. Reducing conditions, such as are obtained with stannous chloride, immobilise the iridium and permit its separation from the mobile platinum and palladium. If the experimental conditions are insufficiently strongly oxidising or reducing, the chromatographic behaviour of iridium is unsatisfactory. It is noteworthy that both the cellulose and the solvent used, hexone (*iso*butyl methyl ketone), are liable partly to reduce iridium.

Solvents—

In the separation procedures described, two solvent mixtures are used, *i.e.*, an acid solvent and an oxidising solvent. The former is hexone containing 3 per cent. v/v of concentrated hydrochloric acid and the latter is, essentially, the acid solvent with the addition of chlorine dioxide. The oxidising solvent is prepared by adding 100 ml of hexone containing 4 per cent. v/v of concentrated hydrochloric acid to a mixture of 4 g of sodium chlorate and 12 g of cellulose powder; the cellulose adsorbs the water formed by the reaction. The solvent (generator solvent) is decanted from the cellulose and then mixed with an equal volume of hexone containing 4 per cent. v/v of concentrated hydrochloric acid. Under these conditions, even after allowance has been made for the acid consumed in the reaction with the sodium

* Part XVI of this series appeared in *J. Appl. Chem.*, 1954, **4**, 539.

chlorate, the hydrochloric acid content of the mixed oxidising solvent cannot fall below 2 per cent. v/v.

The elution behaviour of the complex chlorides of the non-volatile platinum metals with such solvent systems can be summarised by considering the steps involved in the separation of a four-component mixture of platinum, iridium, palladium and rhodium. Under oxidising conditions, platinum, iridium and zinc (a necessary addition, see later) move together in a fairly wide diffused band and are collected as one fraction. The slower-moving palladium is then collected as a second fraction. Rhodium is almost immobile with both oxidising and reducing solvents, but it can be readily eluted with water. Platinum and iridium must be separated on a second column, the iridium being reduced with stannous chloride and the platinum eluted with the acid solvent. The iridium is finally recovered by elution with water.

Experimental

For all separations the platinum metals were initially present as solutions of their complex chlorides in a limited amount of hydrochloric acid. Hexone was added to form a solvent solution for column separation. The preparation of such sample solutions frequently involves the evaporation to dryness of hydrochloric acid solutions of the platinum metals. This often causes the formation of insoluble platinum compounds, and there is evidence that iridium is similarly affected. The addition of sodium chloride prevents this partial insolubility, but tends to have a deleterious effect on the subsequent chromatographic separation. Mercuric chloride has been successfully used with mixtures, such as iridium and rhodium, that are to be separated under oxidising conditions, and it possesses the advantage of being volatile at the temperature of ignition of the platinum metals. Mercuric chloride cannot be used under reducing conditions as it is reduced to metallic mercury, which coats the walls of the vessels and tends to clog the column. Zinc chloride has proved to be generally satisfactory for preventing the partial insolubility of platinum and iridium. It is precipitated in alkaline solutions, but the addition of hydrazine dihydrochloride to precipitate the platinum re-acidifies the solution, and the zinc re-dissolves as chloride.

The separation of the platinum metals from hydrolytic precipitates, *e.g.*, iron, nickel, zinc and copper, in faintly alkaline solution is carried out by the addition of sodium nitrite, which forms nitrite complexes with the platinum metals.[2] To be fully effective, the weight of base metals present should be less than the weight of platinum metals. The palladium - nitrite complex is unstable above pH 10, which makes its separation by this procedure difficult. As palladium is always obtained free from base metals in the chromatographic separation, it can be directly precipitated from acid solution with dimethylglyoxime.

Preparation of the cellulose columns—

The glass extraction tube was of the standard Chemical Research Laboratory design.[3] Burstall and Wells have described the preparation of the cellulose column; the only modifications necessary are described below.

Short columns (15 cm) were found to be adequate for two-component systems in which one component was immobile or nearly immobile, use of such short columns being economical in terms of both time and solvent consumption. Short columns were used to separate platinum, palladium or iridium from rhodium, and also platinum from iridium. Longer columns (30 cm) were needed to separate other two-component systems and when separating three or four-component systems.

Fine grade Whatman ashless cellulose powder was used throughout, and the columns were equilibrated by passing about 5 ml of acid solvent per cm of cellulose-column height through them before commencing a separation. When oxidising conditions were required, a minimum of 50 ml of oxidising solvent was used to equilibrate the column before the solution of the platinum metals was transferred to it.

Separation of base metals—

The presence of base metals lengthens the assay of any individual platinum metal and their prior separation is desirable. The nitrite procedure[2] for the separation of base metals has been found to be satisfactory when the total weight of platinum metals exceeds that of the base metals, but the accuracy of the separation is lowered when the reverse circumstances apply. Adsorption of the platinum metals takes place on the hydrolytic precipitates of the

base metals formed when the solution of the nitrite complexes of the platinum metals is made alkaline, and, if this precipitate is bulky, double precipitation fails to recover the platinum metals quantitatively. In this respect the final determination of platinum is more difficult than that of palladium, iridium or rhodium.

A number of metals, including ferric iron, copper and zinc, are found in the platinum fraction when oxidising conditions are used. Nickel is immobile at the top of the column and is eluted, together with rhodium, by water. Mercuric chloride is mobile and moves with the iridium when the metal is separated from rhodium under oxidising conditions. When reducing conditions apply, stannous chloride is found in the platinum metal fraction together with the chlorides of copper and zinc. Ferrous chloride and reduced iridium remain almost immobile at the top of the column.

In the separation of tin from platinum, the bulk of the tin was removed as stannic chloride by distillation from hydrochloric acid. This procedure was followed by a nitrite separation to ensure that no tin accompanied platinum when the latter was reduced with hydrazine dihydrochloride.

Method

Reagents—

Oxidising solvent—Prepare as described on p. 356.
Acid solvent—Prepare as described on p. 356.
Chlorine.
Stannous chloride.

Procedure for the separation of platinum, palladium, iridium and rhodium—

Bring the platinum metals, present as their acid chlorides, to their fully oxidised states and add sufficient zinc chloride to ensure that the weight of zinc is at least equal to the combined weights of the platinum and iridium. If nitric acid is present, evaporate the sample to dryness on a steam-bath and then repeatedly evaporate the residue with small portions of concentrated hydrochloric acid. Add a few millilitres of dilute hydrochloric acid and saturate the solution with chlorine. Evaporate again, avoiding any overheating of the residue, and remove excess of acid and condensate from the walls of the beaker at as low a temperature as possible. Dissolve the residue in 1·0 ml of concentrated hydrochloric acid saturated with chlorine, add 10 ml of generator solvent and then 10 ml of hexone. Replace each withdrawal of solvent by the addition to the generator of the same volume of hexone containing 4 per cent. v/v of concentrated hydrochloric acid and stir the mixture. The initial acidity of the sample solution is rather high, but it decreases as the elution proceeds. It is important to limit the initial volume of the sample solution and the solvent washings of the sample beaker. If the total volume of sample solution is too great, chromatographic separation commences before the last of the platinum-bearing solution comes into contact with the cellulose. If a few drops of aqueous phase separate from the solvent solution of the sample, this aqueous phase should be retained in the beaker by careful decantation of the solvent and the solvent washings. Some of the rhodium present in the sample will remain in the aqueous phase and is indicated by a characteristic rose-red colour. The remaining rhodium is immobile at the top of the column and is indicated by a narrow red band.

Allow the level of the sample solution to fall to the top of the cellulose column, and then rinse the beaker with successive 3 to 4-ml portions of oxidising solvent, any aqueous phase being retained in the beaker. The volume of washing solvent must be kept to a minimum. Elute the mixture by addition of oxidising solvent, care being taken to ensure that the level of the solvent does not fall below the top of the cellulose column.

A wide diffuse band of iridium moves rapidly down the column, its brown colour masking the presence of some platinum that moves with it, sometimes a little ahead, but not detached from the iridium band. The bulk of the platinum follows the iridium as an adjacent merging band. As elution proceeds, the deep yellow platinum band moves completely away from the fairly compact orange-brown palladium band. Palladium moves away from the immobile rhodium, but at a much slower rate than does the wide platinum - iridium band.

Platinum and iridium are collected as a single fraction of about 200 to 250 ml in a 500-ml round-bottomed flask fitted with a ground-glass joint to facilitate subsequent distillation. Zinc and any iron and copper present will move with the platinum and iridium, but any nickel present will be retained at the top of the column together with the rhodium. To avoid

any loss of iridium from the platinum - iridium fraction, the palladium band is allowed to approach the bottom of the column before the palladium fraction is collected. Fully oxidising conditions must be maintained to prevent any retention of iridium in the palladium band.

The palladium fraction is collected in a similar 500-ml round-bottomed flask, and the addition of solvent to the column is discontinued as soon as all the palladium has been eluted; the palladium fraction is usually about 100 to 150 ml.

Transfer any rhodium remaining in the sample beaker to the column with a jet of distilled water and acidify the aqueous solution with a few drops of dilute hydrochloric acid. Since both rhodium and nickel move rapidly down the column, the major proportion of the oxidising solvent remaining in the column should be run either into the palladium fraction or to waste, otherwise the aqueous rhodium fraction will be accompanied by an inconveniently large volume of solvent. Collect the rhodium fraction, about 100 ml, in a 250-ml beaker and evaporate the layer of solvent under an infra-red lamp.

Separation of platinum from iridium—Add water to the flask containing the first fraction and fit a Claisen head and condenser. Pass a current of air through a fine capillary reaching almost to the bottom of the flask and distil the solvent and a limited amount of water. Transfer the remaining aqueous solution to a 150-ml beaker and remove any carbonaceous deposit (resulting from breakdown of the solvent) from the walls of the flask with hot aqua regia. Add the acid solution to the beaker and evaporate the mixture to dryness, finishing on a steam-bath. Repeatedly evaporate the residue with small portions of concentrated hydrochloric acid to ensure the complete removal of nitrate in conditions that avoid overheating the residue. Dissolve the residue in 1·0 ml of concentrated hydrochloric acid, add 200 mg of stannous chloride and dissolve the solid by gentle agitation. Add 20 ml of hexone to the solution, which is highly coloured owing to the formation of an orange-red tin - platinum complex. This complex is unstable in solvent solution, but, if it does not break down in the cold with the production of the characteristic yellow colour of chloroplatinic acid, heat the contents of the beaker for a few seconds on a steam-bath to accelerate the decomposition.

Equilibrate a 15-cm cellulose column with the acid solvent and decant the reduced platinum - iridium mixture on to it, avoiding the transfer of any of the aqueous phase. Rinse the beaker repeatedly with 3 to 4-ml portions of solvent and transfer the washings to the column, still retaining the aqueous phase. Collect the platinum fraction in a 500-ml round-bottomed flask and remove the solvent by distillation as described above, transferring the aqueous solution and acid washings of the flask to a 400-ml beaker. Elute the reduced iridium from the top of the column by addition of the faintly acidified water used to rinse the sample beaker in the same way as that described for the elution of rhodium. Collect the iridium solution in a 400-ml beaker and evaporate the solvent.

At this stage, the four platinum metals are quantitatively separated and the assay methods selected will depend on the identity and concentration of any base metals present. Palladium is free from such contamination and can be precipitated as the dimethylgloxime complex.

Evaporate the aqueous platinum solution to small volume, add concentrated hydrochloric acid and then remove tin by distillation as stannic chloride, assisted by the addition of bromine to the hydrochloric acid solution. After evaporation of the chloride solution to dryness, determine platinum by the standard method[2] of precipitation of the metal by reduction with hydrazine dihydrochloride; determination of platinum by this method has proved to be satisfactory in the presence of copper and zinc. The remaining platinum metals can also be determined by standard procedures,[2] iridium by bromate hydrolysis and rhodium by precipitation with hydrazine dihydrochloride.

PROCEDURES FOR THE SEPARATION OF TWO-COMPONENT MIXTURES—

The description of the method for the separation of the four non-volatile platinum metals will clarify the chromatographic behaviour of these metals in the solvent systems recommended, and the general requirements for the separation of any pair will be fairly clear. Some two-component systems are described, however, with the intention of amplifying certain details.

Separation of iridium from rhodium—Add 250 mg of mercuric chloride to the hydrochloric acid solution of the metal chlorides contained in a 150-ml beaker and evaporate to dryness on a steam-bath. Add a few millilitres of dilute hydrochloric acid, saturate the solution with chlorine and again evaporate to dryness. Dissolve the residue in 1·0 ml of concentrated

hydrochloric acid saturated with chlorine, add 10 ml of generator solvent and then 10 ml of hexone. Use a 15-cm cellulose column equilibrated with solvent and pass through a minimum of 50 ml of oxidising solvent before decanting the sample solution on to the column. Retain any aqueous phase and rinse the beaker with successive 3 to 4-ml portions of oxidising solvent. Maintain oxidising conditions throughout the separation to prevent any retention of trace amounts of iridium. Collect the iridium fraction in a 500-ml round-bottomed flask and elute the rhodium with water.

Separation of rhodium from other platinum metals—Use the oxidising solvent even in the absence of iridium, since it is desirable to repress the formation of any slower-moving reduction product of platinum. Use a 15-cm column for the separation of rhodium from platinum or palladium, but a 30-cm column for the separation of all three metals.

Separation of palladium from iridium—Use a 15-cm column and maintain oxidising conditions throughout to keep iridium moving away from the less mobile palladium. A separation based on the retention of reduced iridium will fail because of the marked effect of reduction on the chromatographic behaviour of palladium.

Separation of platinum from iridium—This separation has already been described, but it is noteworthy that, under the reducing conditions that apply in this instance, the chromatographic behaviour of platinum differs from its behaviour under fully oxidising conditions. When the platinum - iridium mixture has been reduced by stannous chloride and the solvent solution transferred to the column, the platinum invariably divides into two forms. A wide mobile yellow band accounts for most of it, and a slow-moving dull pink band represents the remainder. The two bands may separate, but both should be collected in one fraction. Sufficient solvent should be used to remove all trace of the less mobile product before commencing to elute iridium with water. Water elutes iridium very rapidly.

If a relatively large amount of platinum is being separated from a trace of iridium, it may be impossible to detect the presence of iridium at the top of the column by visual inspection. An operator unfamiliar with the characteristic colours of the various platinum metal complexes could mistake the slow-moving platinum band for iridium and collect it as such in a separate fraction. Iridium would then be rejected with the column packing, part of the platinum would be reported as iridium and the value found for platinum would be less than the true one. If sufficient iridium is present to be plainly seen at the top of the column, its colour is a dull greyish green; it cannot be confused with the dull pink of the slow-moving platinum band.

Separation of platinum from palladium—Use a 30-cm column and oxidising conditions throughout the separation.

Results of chromatographic separations

Table I shows the assay results of separations in which both the components and the concentrations were varied. It is considered that such discrepancies as exist were due to errors in assay rather than to any defect in the separation procedures. Gravimetric methods by standard procedures[2] were used in the majority of the determinations, palladium being weighed as the dimethylglyoxime complex, and the other platinum metals as the metallic residue obtained by ignition in a stream of hydrogen. Worcester porcelain crucibles 4 cm in diameter were used, with Rose-type quartz covers with a central hole for the delivery of hydrogen from a quartz delivery tube. After ignition in hydrogen, leaching with hot dilute hydrochloric acid to remove occluded sodium and re-ignition in hydrogen, the residues were cooled in a stream of carbon dioxide and weighed on a semi-micro balance.

Micro methods were used in the determination of amounts of platinum metal too low to be accurately assessed by a gravimetric procedure.

The high platinum recovery in experiment 3 is due to the occlusion of iron in the reduced metal. In early experiments, iridium was reduced in the sample solution by passing sulphur dioxide through it, and a trap, consisting of a mixture of cellulose powder and solid ferrous sulphate, was placed at the top of the column in an attempt to maintain reducing conditions. Some oxidation of iron occurred with the result that iron appeared in the solvent fraction containing platinum and in the aqueous iridium fraction. This, in itself, is not a serious objection, but it was found that reduction of iridium by sulphur dioxide in the sample solution was frequently difficult or incomplete, hence it was decided to reduce the iridium with stannous chloride and to dispense with the trap.

TABLE I

RECOVERY OF THE NON-VOLATILE PLATINUM METALS BY THE PROPOSED METHOD

Experiment No.	Platinum present, mg	Platinum found, mg	Palladium present, mg	Palladium found, mg	Iridium present, mg	Iridium found, mg	Rhodium present, mg	Rhodium found, mg
1	98·40	98·26	—	—	—	—	0·87	0·86
2	4·94	4·50	—	—	—	—	107·8	107·9
3	98·40	99·42	—	—	1·02	0·98	—	—
4	—	—	50·45	50·10	—	—	54·12	53·59
5	98·14	98·60	—	—	4·70	4·90	—	—
6	—	—	48·45	48·17	—	—	57·07	56·90
7	—	—	—	—	4·70	4·62	114·1	114·0
8	—	—	—	—	52·23	52·39	5·71	5·79
9	98·40	98·12	5·75	5·4	5·06	5·12	5·7	5·9
10	49·20	50·35	57·11	57·57	49·12	49·66	57·6	57·3
11	23·03	22·72	19·38	18·91	19·83	19·61	22·83	22·96
12	197·2	197·1	0·97	1·02	—	—	—	—
13	95·85, 95·6, 95·64	95·24, 95·70	0·55, 0·56, 0·55	0·53	—	—	—	—
14	95·25, 94·9, 94·73	94·23, 94·16	0·35, 0·45 to 0·7, 0·38	0·42	at least 0·24	0·42, 0·44	—	—

In experiments 1 and 3, rhodium was determined photometrically and iridium by a micro-titration method described elsewhere.[1]

Base metals were included in the sample for separation in experiment 11. These were added as chlorides equivalent to 100 mg of zinc and 20 mg each of copper, nickel and iron. The results show that the presence of limited amounts of these metals has no influence on the chromatographic behaviour of the platinum metals.

Experiment 12 is typical of the analysis of a platinum-base alloy containing a small amount of palladium; a small amount of copper was also included.

Experiments 13 and 14 show the results of analysis of platinum-base alloys supplied by the Assay Office, Goldsmith's Hall. The figures shown in the "present" columns of Table I are the values submitted by the Assay Office and are regarded as reliable. In experiment 13, platinum was alloyed with small amounts of copper, palladium and gold, and in experiment 14, the platinum was associated with copper, palladium, gold, iridium and rhodium.

CONCLUSIONS

The proposed procedures provide rapid and simple methods for the quantitative separation of the non-volatile platinum metals. The apparatus required is limited and simple in design, and, by following the methods described, the manipulator should experience no difficulty in separating the characteristically coloured bands of the platinum metals.

The chromatographic analyses of platinum-base alloys agree well with those submitted by other laboratories (the Assay Office and the Mond Nickel Company), who use different methods of separation and assay. Separations on a larger scale have not been undertaken, but no difficulties are foreseen in dealing with much greater amounts of the platinum metals.

We thank the Deputy Warden, Assay Office, Goldsmith's Hall, for samples of platinum-base alloys and for his permission to publish the results of analyses. Frequent references have been made to "The Analysis of Minerals and Ores of the Rarer Elements."[2] The section devoted to the platinum metals has been of value in problems connected with assay.

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Spectrochemical Methods of Analysis as Applied to Mineral Matter Associated with Coal

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An account is given of the application of spectrochemical solution techniques to the analysis of mineral matter associated with coal. Solutions are prepared by fusing the sample and then extracting the melt, or by wet oxidation. Calibration for the major constituents, silicon, aluminium, iron, calcium, magnesium, sodium and potassium, and the minor constituents, titanium, manganese, copper, strontium and barium, is carried out with synthetic standards prepared, whenever possible, from Specpure materials. Sodium and potassium are determined with a flame photometer. The techniques are appreciably faster than other published methods, and have a comparable precision. They are applicable to gas producer and cyclone burner slags, as well as to coal ash.

THE intensive use of coal in modern industrial appliances for combustion and gasification is bringing to light many new problems in the behaviour of the mineral matter associated with coal and coal seams, and a better knowledge of the composition and behaviour of this mineral matter is urgently needed. Interest centres chiefly on the major rather than the trace constituents, and the current paucity of information is a measure of the difficulty and length of the classical methods of chemical analysis, which have, until recently, been regarded as standard methods. Within the last few years, three papers[1,2,3] have been published that describe rapid colorimetric and composite schemes of analysis; the methods proposed are some four or five times as rapid as the classical methods[4] and are of acceptable precision, the coefficient of variation of the determination of a major constituent being approximately 2 per cent. Spectrochemical methods are potentially several times more rapid than the recently published methods and the aim of this investigation has been to devise a suitable spectrochemical procedure and to assess its precision, speed and range of applicability.

Experimental

Preparation of solutions—

Samples may be received as coal, coal ash, or extracts in acid or aqueous media. Solutions of coal or ash can be prepared by wet oxidation or by fusion and then extraction of the melt with water or acid.

Wet oxidation is particularly useful when coal and dirt bands that have high contents of organic matter are to be analysed without recourse to ashing. In such instances, the silica must be determined gravimetrically and any residue after its removal as tetrafluoride must be fused, extracted and the extract added to the original filtrate.

The most convenient approach, however, is to ash the sample according to the British Standard procedure[5] and then to proceed by means of a fusion technique—information about the ash content of a sample is usually required. A separate solution, prepared by digestion with a mixture of hydrofluoric and sulphuric acids to ensure complete breakdown of silicate materials, is then used for the determination of the alkali metals.

Clay minerals and slags are treated in the form in which they are received, carbon dioxide, moisture at 105° C, water of constitution, sulphur, carbon and phosphorus being determined chemically to complete the analysis.

When an exceptionally high concentration of an element is likely to occur, sample weights of less than 0·1 g are usually taken.

Chromium was chosen as the internal standard to be added to each solution. This element gives a useful number of spectral lines in the wavelength range 2500 to 4600 A and occurs only in trace amounts in coal ash and associated clay minerals.

Excitation—

Three methods are most frequently used to introduce solutions into a discharge gap, namely, the Feldman porous cup, the rotating graphite wheel and a method in which the

solution is absorbed by a porous graphite electrode before sparking, see Fig. 1. The last-named was chosen because of its ease of preparation, the small amount of high-purity electrode required and its availability for the possible future determination of trace elements by means of an arcing technique.

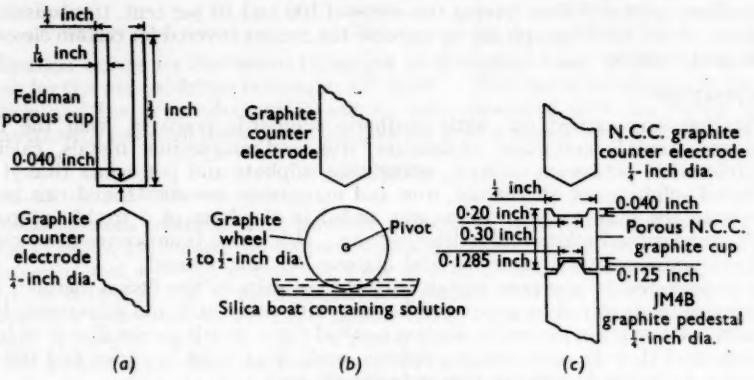

Fig. 1. Types of electrodes used for the analysis of solutions

The small sections of high-purity graphite electrodes were packed into a shallow fused silica dish and made porous by heating at 800° C for 15 minutes. Spectra were produced with an uncontrolled condensed-spark discharge. Such a source unit gives one or more heavily damped discharges across the analytical gap per half cycle of the supply frequency. The peak current of an individual discharge is about 100 amperes.

The operating conditions finally chosen were as follows—

Spectrograph—	Hilger large quartz.
Spark gap—	2·5 mm.
Voltage across the gap, r.m.s.—	15,000 volts.
Added inductance—	0·015 mH.
Capacitance—	0·005 μF.
Upper electrode—	N.C.C. graphite electrode, having a 40° cone with a 1 mm flat.
Lower electrode—	N.C.C. graphite electrode, having a crater 0·04 inch deep and 0·20 inch in diameter.
Slit width—	0·020 mm.
Source to slit distance—	38 cm; image formed at collimating lens.
Exposure—	2 superimposures, each of 50 seconds.
Plate—	Ilford special rapid.

By making two superimposures, the use of salt solutions of concentrations greater than 4 per cent., which would crystallise on the top of the lower electrode on sparking, was avoided, and a smaller sample could be used. This is an important consideration when coal is analysed in the form of air-borne dust.

PHOTOGRAPHIC CONSIDERATIONS—

Control of the photographic processes is maintained by plate calibration using the iron-line group method, see Table I. The slope of the emulsion-characteristic curve, gamma, is obtained from a plot of the Seidel function of density against the relative intensity of each iron line. Tables were prepared to convert densitometer scale units directly to relative intensity for values of gamma within the range 1·05 to 1·20 in steps of 0·03.

TABLE I

RELATIVE INTENSITIES OF THE IRON-LINE GROUP

Wavelength, A	..	2783·7	2793·9	2799·3	2812·5	2819·3	2823·3	2827·4	2828·6	2831·6	2835·5
Relative intensity	..	8·30	1·39	1·00	0·15	0·19	0·69	0·43	1·09	4·73	2·57

All spectrum-line readings are corrected for background, a single measurement in the vicinity of the analytical line being applied to both this and the control line. After correction, calibration curves are linear over at least a hundred-fold concentration range.

For line pairs of wavelength greater than 3400 A, plate calibration is by means of a rotating-sector spectrogram of an iron - carbon arc.

A rhodium-sputtered filter having two steps of 100 and 10 per cent. transmission can be used in front of the spectrograph slit to increase the ranges covered for certain elements, *e.g.*, strontium and barium.

STANDARDISATION—

Calibration was carried out with synthetic standards prepared from the following Specpure and AnalaR materials: aluminium, iron and magnesium metals, calcium and sodium carbonates, potassium chloride, manganese sulphate and potassium titanyl oxalate. The hydrated sulphates of aluminium, iron and manganese are stable, and can be used as alternatives to the pure metals. Silica was added in the form of a freshly prepared and chemically standardised solution of sodium silicate. When this is not convenient, chemically standardised samples such as coal ash and diabase W1 can be used.

If it is preferred to use pure metals rather than salts in the fusion method, iron and magnesium can be dissolved by prolonged heating with nitric acid and aluminium by fusion with sodium hydroxide; in the wet-oxidation method these metals can be dissolved in diluted hydrochloric acid (1 + 1), after which sulphuric acid, sp.gr. 1·84, is added and the solution is evaporated to fumes to remove the hydrochloric acid.

Standards for calibration were prepared from two solutions, both of which contained 20 ml of internal-standard solution per 25 ml, acid and fusion mixture when appropriate, and one of which contained also the maximum concentrations of the elements to be determined. The two solutions were mixed to give a series of six standards with a dilution factor of two.

Calibration curves were plotted from the mean of quintuplicate spectrograms for each standard on each of four plates, thereby permitting the precision of the technique at different concentration levels to be found.

The chosen line pairs, together with the concentration ranges covered and limits of detection, are given in Tables IIA and IIB.

TABLE IIA

SPECTROPHOTOMETRIC DATA

Element	Line pair, A	Excitation potential, eV	Concentration range covered, %	Sensitivity, %
Silicon	Si I 2881·6 - Cr I 3021·6	5·1 —	1·0 to 60·0	<0·50
Aluminium ..	Al I 3082·2 - Cr I 3021·6	4·0 —	1·0 to 40·0	0·20
Iron	Fe II 2755·7 - Cr II 2757·7	13·3 12·6	1·0 to 50·0	0·10
Calcium	Ca II 3179·4 - Cr II 3180·7	13·1 13·1	0·25 to 20·0	0·10
Magnesium ..	Mg II 2802·7 - Cr II 2757·7	12·0 12·6	0·02 to 2·0	0·002
	Mg II 2798·0 - Cr II 2757·7	— 12·6	0·50 to 10·0	—
Titanium	Ti II 3349·0 - Cr II 3180·7	11·1 13·1	0·20 to 2·0	0·05
Manganese	Mn 2933·1 - Cr 2935·1	12·8 —	0·10 to 2·0	0·05
Copper	Cu I 3247·5 - Cr I 3021·6	3·8 —	0·10 to 5·0	0·05
Strontium	Sr II 4077·7F - Cr I 4289·7F	8·7 2·9	0·05 to 0·50	0·02
Barium	Ba II 4554·0 - Cr I 4289·7	7·9 2·9	0·05 to 5·0	0·02

F = filtered portion of the line.

TABLE IIB

FLAME-PHOTOMETRIC DATA

Element	Wavelength of line or band, A	Concentration range, p.p.m.
Sodium	5890	0·0 to 4·0
Potassium	7665	0·0 to 6·0

Calibration curves for the fusion technique have slightly lower slopes, 42° to 44°, than have those for the wet-oxidation technique, 43° to 45°. This can be attributed to the different acid radicle and the preponderance of sodium ions associated with the fusion technique. The elements with low excitation potentials give the lowest slopes, whichever method is used.

METHOD

PREPARATION OF SOLUTIONS—

Internal-standard solution—This solution is prepared from chromium trioxide that has been dried at 105° C for 1 hour, and contains 0·3846 g per 200 ml of 12 per cent. v/v nitric acid.

Solution of coal ash—Approximately 0·1 g of ash, ground to pass through a 240-mesh B.S. sieve, is heated to 775° C for 30 minutes to remove moisture and carbon dioxide; it is then cooled in a desiccator, weighed and transferred to a platinum crucible of capacity 30 ml. The sample is covered with 1 ± 0·05 g of fusion mixture (5 parts of anhydrous sodium carbonate and 3 parts of pre-fused sodium borate) and gently heated for 1 to 2 minutes, then for a further 2 to 3 minutes at a dull red heat (450° to 550° C) and finally in the flame of a Meker burner at full heat (900° to 1000° C) for 5 minutes to ensure complete fusion. When cool, 20 ml of internal-standard solution are added and then 5 drops of 90 to 100-volume hydrogen peroxide to retain manganese and titanium in solution. The crucible lid is washed with 5 ml of 12 per cent. v/v nitric acid, the washings being added to the solution. The cold solution is then stirred mechanically for 10 to 15 minutes to complete the extraction.

Note that care is needed in the extraction to prevent the precipitation of silica, which may occur if the temperature is above 50° C or if the stirring is inadequate. Even in the presence of a citric acid - sodium citrate buffer solution,[6] temperatures above 70° to 80° C are not recommended.

The solutions have a final volume of 25 ± 1 ml; greater precision is not required in a ratio method. They should preferably be used within 3 hours of preparation, as when they are set aside for longer than 6 hours barium may separate as barium sulphate and there is some risk of silica also being precipitated.

Solution for alkali determination—When the above-described procedure is used to prepare a solution of ash, alkalis are determined on a separate 0·1-g sample. This is weighed into a platinum crucible of capacity 30 ml, 6 ml of 50 per cent. v/v sulphuric acid and 5 ml of 40 per cent. w/w hydrofluoric acid are added, and the mixture is heated until fumes of sulphur trioxide are evolved and held at that stage for 15 minutes. When cool, the solution is quantitatively transferred to a 100-ml calibrated flask, diluted to the mark and set aside for 1 hour.

Wet oxidation of coal—A 1-g sample of air-dried coal (2 g if the ash content is 5 per cent.) is ground to pass through a 72-mesh sieve and then weighed into a 250-ml tall beaker. Fifteen millilitres of nitric acid, sp.gr. 1·42, are added and the beaker is strongly heated for 15 minutes, more nitric acid being added when required to prevent baking of the sample. This preliminary treatment destroys much of the organic matter, and also reduces the frothing that occurs when sulphuric acid is added. When cool, 3 ml of sulphuric acid, sp.gr. 1·84, and 2 ml of nitric acid, sp.gr. 1·42, are added and the solution is then heated until fumes of sulphur trioxide are evolved, this procedure being repeated after each addition of nitric acid. After removal of the organic matter, indicated by the pale straw colour of the solution, 5 ml of 72 per cent. perchloric acid are added, and subsequently removed by evaporation, to leave the silica in a form that can be readily removed by filtration. When cool, the walls of the beaker are washed with 20 to 30 ml of hot water and the solution is again evaporated to fumes. A further addition of 20 to 30 ml of water is made in washing the walls of the beaker, the solution is brought to a gentle boil and then filtered hot through an 11-cm Whatman No. 542 filter-paper. If the residual silica is slightly coloured due to absorption of iron, the oxidation should be repeated on a fresh sample, as the iron cannot be recovered by washing.[7]

Table IV

Comparison of the proposed fusion method with classical chemical methods

Analyses by chemical methods[4] were carried out at the British Coal Utilisation Research Association. In all instances the alkalis were determined by flame-photometric methods

	SiO_2 found by—			Al_2O_3 found by—			Fe_2O_3 found by—			CaO found by—		
Sample No.	chemical method, %	fusion method, %	Difference, %	chemical method, %	fusion method, %	Difference, %	chemical method, %	fusion method, %	Difference, %	chemical method, %	fusion method, %	Difference, %
2461*	21·5	21·0	−0·5	18·8	19·8	+1·0	38·9	39·3	+0·4	6·7	6·8	+0·1
2860†	47·4	48·2	+0·8	25·8	24·5	−1·3	8·6	9·0	+0·4	9·8	10·0	+0·2
2869*	36·7	36·5	−0·2	20·2	20·2	0·0	17·0	17·8	+0·8	11·5	12·1	+0·6
3034*	44·0	44·2	+0·2	22·6	23·4	+0·8	11·6	11·1	−0·5	7·3	7·8	+0·5
3341‡	38·0	37·2	−0·8	25·3	24·7	−0·6	12·1	11·9	−0·2	10·4	10·9	+0·5
3343*	48·2	47·9	−0·3	29·6	29·0	−0·6	5·8	5·6	−0·2	6·7	7·2	+0·5
3344‡	47·5	48·3	+0·8	29·0	29·0	0·0	5·9	5·8	−0·1	5·3	5·4	+0·1
3345*	48·9	48·2	−0·7	23·2	24·0	+0·8	6·6	6·1	−0·5	10·5	10·8	+0·3
3346‡	46·1	46·5	+0·4	24·0	24·7	+0·7	11·2	11·2	0·0	5·9	6·0	+0·1
3360*	54·4	54·7	+0·3	24·7	23·8	−0·9	10·1	9·9	−0·2	2·4	2·3	+0·1
3446†	51·5	51·7	+0·2	28·2	28·6	+0·4	6·0	5·8	−0·2	7·9	7·7	+0·2
3450†	44·9	44·1	−0·8	27·1	26·9	−0·2	16·3	15·9	−0·4	3·4	3·2	+0·2
Diabase W1	52·6	53·2	+0·6	15·2	14·6	−0·6	10·9	11·0	+0·1	10·9	10·9	0·0

	MgO found by—			TiO_2 found by—			Na_2O found by—			K_2O found by—		
Sample No.	chemical method, %	fusion method, %	Difference, %	chemical method, %	fusion method, %	Difference, %	chemical method, %	fusion method, %	Difference, %	chemical method, %	fusion method, %	Difference, %
2461*	3·9	3·8	−0·1	0·5	0·5	0·0	1·1	1·0	−0·1	0·5	0·5	0·0
2860†	3·5	3·2	−0·3	0·7	0·9	+0·2	0·8	0·7	−0·1	3·2	3·1	−0·1
2869*	5·0	4·9	−0·1	0·6	0·6	0·0	0·8	0·4	−0·4	2·8	2·9	+0·1
3034*	3·2	3·0	−0·2	0·7	0·8	+0·1	3·0	3·0	0·0	3·4	3·5	+0·1
3341‡	2·3	2·0	−0·3	1·2	1·2	0·0	4·3	4·2	−0·1	0·6	0·8	+0·2
3343*	1·3	1·1	−0·2	0·9	0·9	0·0	1·0	1·0	0·0	3·8	3·7	−0·1
3344‡	1·3	1·2	−0·1	1·1	1·1	0·0	1·6	1·6	0·0	4·4	4·4	0·0
3345*	1·6	1·4	−0·2	0·9	0·9	0·0	1·7	1·6	−0·1	3·5	3·4	−0·1
3346‡	1·6	1·5	−0·1	1·1	1·1	0·0	2·8	2·7	−0·1	3·8	3·8	0·0
3360*	1·8	1·5	−0·3	1·1	1·0	−0·1	0·6	0·5	−0·1	3·4	3·3	−0·1
3446†	2·3	2·2	−0·1	1·0	0·9	−0·1	0·3	0·3	0·0	2·8	2·9	+0·1
3450†	2·5	2·3	−0·2	0·8	0·8	0·0	0·5	0·4	−0·1	3·1	3·2	+0·1
Diabase W1	6·6	6·4	−0·2	1·1	1·1	0·0	2·1	2·0	−0·1	0·7	0·7	0·0

* Coal ash prepared at 775° C. † Slag. ‡ Flue dust.

TABLE V

COMPARISON OF THE PROPOSED FUSION AND WET-OXIDATION METHODS WITH A CHEMICAL METHOD

The samples used were coal ash, prepared at 380° C. The chemical analyses were carried out by a colorimetric semi-micro method[3] with use of the same solvent acids as in the wet-oxidation method

Sample No.	SiO_2 found by—		Al_2O_3 found by—			Fe_2O_3 found by—			CaO found by—		
	chemical method, %	fusion method, %	chemical method, %	wet-oxidation method, %	fusion method, %	chemical method, %	wet-oxidation method, %	fusion method, %	chemical method, %	wet-oxidation method, %	fusion method, %
3622	36·6	37·3	28·3	29·2	29·2	4·75	5·00	4·80	8·8	9·5	9·2
4761	31·0	31·7	24·3	23·4	23·8	6·3	6·5	6·3	11·7	11·8	12·8
4731	35·0	35·1	26·6	26·1	27·1	5·50	5·65	5·50	9·7	9·4	9·8
18443	36·7	37·7	28·4	28·5	28·6	4·95	5·00	5·00	8·1	8·5	8·6
18444	29·1	20·4	23·3	23·2	23·5	6·6	6·8	7·1	13·2	13·3	14·4
47H50	20·7	20·3	16·7	16·3	16·8	43·0	42·9	44·1	3·95	4·45	4·05
48H50	21·9	21·8	13·4	12·7	12·8	19·9	19·3	20·5	14·0	14·4	14·9
49H50	19·7	20·8	16·6	15·8	16·5	23·8	22·7	23·7	11·4	11·8	12·1
252H50	24·2	23·8	19·9	19·3	20·4	9·2	9·2	9·4	11·3	11·5	11·9
54/275	17·7	18·2	9·5	9·6	10·0	43·6	42·9	44·5	5·10	4·80	4·60
45/4	24·7	25·1	26·4	26·0	27·0	9·8	9·5	9·6	12·2	12·0	13·7

Sample No.	MgO found by—			TiO_2 found by—			Mn_3O_4 found by—		
	chemical method, %	wet-oxidation method, %	fusion method, %	chemical method, %	wet-oxidation method, %	fusion method, %	chemical method, %	wet-oxidation method, %	fusion method, %
3622	1·90	1·96	1·91	0·81	0·79	0·80	0·21	0·25	0·18
4761	2·76	2·45	2·50	0·76	0·77	0·75	0·34	0·32	0·33
4731	2·26	1·92	1·80	0·78	0·75	0·74	0·24	0·21	0·23
18443	1·92	1·86	1·82	0·80	0·80	0·83	0·24	0·23	0·22
18444	3·60	3·15	3·50	0·68	0·67	0·66	0·44	0·41	0·44
47H50	1·83	1·80	1·84	0·47	0·46	0·45	0·21	0·20	0·20
48H50	3·00	2·77	2·97	0·53	0·52	0·51	0·27	0·26	0·24
49H50	3·95	3·60	4·10	0·52	0·48	0·51	0·41	0·33	0·28
252H50	4·45	4·40	4·65	0·99	0·97	1·03	0·52	0·48	0·49
54/275	0·59	0·56	0·55	0·32	0·30	0·33	0·05	⩽0·15	⩽0·15
45/4	2·54	2·08	2·21	0·63	0·54	0·54	0·14	0·17	0·16

TABLE VI

THE EFFECT OF ASHING ON THE MAJOR CONSTITUENTS

The ashing was carried out by the British Standard procedure.[5] The chemical analyses were carried out by a colorimetric semi-micro method[3] and the spectrochemical analyses by the wet-oxidation method, the same solvent acids being used in both methods. The results for coal samples are calculated on the basis of ash

Sample No.	Original form of sample	SiO_2 found by chemical method, %	Al_2O_3 found by— chemical method, %	Al_2O_3 found by— spectrochemical method, %	Difference, %	Fe_2O_3 found by— chemical method, %	Fe_2O_3 found by— spectrochemical method, %	Difference, %	CaO found by— chemical method, %	CaO found by— spectrochemical method, %	Difference, %
5355	coal	42·0	30·7	29·3	−1·4	6·9	7·6	+0·7	11·5	11·1	−0·4
	ash	41·5	—	30·0	−0·7	—	7·3	+0·4	—	11·8	+0·3
5356	coal	29·7	20·4	19·7	−0·7	43·6	43·6	0·0	1·81	1·80	−0·01
	ash	30·0	—	21·7	+1·3	—	44·7	+1·1	—	1·91	+0·10
5357	coal	28·7	24·7	24·2	−0·5	22·3	22·8	+0·5	14·5	14·3	−0·2
	ash	28·9	—	24·0	−0·7	—	21·6	−0·7	—	14·2	−0·3
5358	coal	36·2	24·9	23·7	−1·2	21·0	20·4	−0·6	7·9	7·6	−0·3
	ash	35·8	—	24·3	−0·6	—	20·7	−0·3	—	7·9	0·0
5359	coal	22·2	18·3	18·0	−0·3	31·0	32·5	+1·5	15·2	15·6	+0·4
	ash	21·7	—	18·9	+0·6	—	31·2	+0·2	—	15·5	+0·3

Sample No.	Original form of sample	MgO found by— chemical method, %	MgO found by— spectrochemical method, %	Difference, %	TiO_2 found by— chemical method, %	TiO_2 found by— spectrochemical method, %	Difference, %	Mn_3O_4 found by— chemical method, %	Mn_3O_4 found by— spectrochemical method, %	Difference, %
5355	coal	3·19	3·20	+0·01	0·98	0·98	0·00	0·37	—	—
	ash	—	3·21	+0·02	—	0·96	−0·02	—	0·41	+0·04
5356	coal	0·81	0·78	−0·03	0·57	0·55	−0·02	0·06	—	—
	ash	—	0·84	+0·03	—	0·56	−0·01	—	⩽0·15	—
5357	coal	5·10	5·25	+0·15	0·69	0·67	−0·02	0·28	—	—
	ash	—	5·10	0·00	—	0·65	−0·04	—	0·26	−0·02
5358	coal	4·2	4·3	+0·10	1·18	1·17	−0·01	0·19	—	—
	ash	—	4·2	0·00	—	1·15	−0·03	—	0·18	−0·01
5359	coal	3·55	3·65	+0·10	0·68	0·68	0·00	0·46	—	—
	ash	—	3·35	−0·20	—	0·69	+0·01	—	0·45	−0·01

The residue is washed with 150 ml of hot water, and, after the addition of 20 ml of internal-standard solution per 25 ml of final volume, the filtrate is evaporated to about 15 to 20 ml before being transferred to a 25-ml calibrated flask and diluted to the mark. For samples containing more than 10·0 per cent. of calcium, the final volume may be 50 ml, as the solubility of calcium sulphate is only about 5 mg per 10 ml.

With this technique the solution is diluted to a known volume to permit a 2-ml aliquot to be taken for the determination of alkalis. Silica is determined by a standard gravimetric procedure. Residues after removal of the silica as tetrafluoride seldom exceed 1 mg, and when they do, they are fused and the extract added to the original filtrate. In these circumstances, another portion of the sample must be dissolved in the same way as for the preparation of the solution for alkali determination.

Acid or aqueous extracts of coal—To such extracts, 3 ml of sulphuric acid, sp.gr. 1·84, are added and the solution is heated to fumes. When cool, 20 ml of internal-standard solution are added and the solution is diluted to 25 ml. All soluble constituents can be determined on this solution, the same calibration curves as for the wet-oxidation technique being used.

EXCITATION PROCEDURE—

A 0·05-ml portion of the prepared solution is added to a porous electrode, see Fig. 1 (*c*). After 40 to 60 seconds in which to dry, the electrode is sparked for 50 seconds against a high-purity graphite counter-electrode. The electrode is then allowed to cool for 10 seconds, after which a second drop of solution is added to it, and a second exposure is superimposed on the first. A duplicate spectrogram is prepared from the same solution, the mean of the two forming a single determination. Duplicate spectrograms for twelve samples can be prepared in 1 hour.

PHOTOMETRIC PROCEDURE FOR ALKALIS—

A 2-ml aliquot of the wet-oxidation solution, or 5 ml of the solution prepared by hydrofluoric - sulphuric acid digestion, is diluted and used for the determination of sodium and potassium by standard flame-photometric procedures; an E.E.L. flame photometer (Evans Electroselenium Ltd.) was used. The two solutions have approximately the same normality with respect to sulphuric acid, so that the same operating conditions can be used for both.

The determinations were found to be unaffected by changes in normality with respect to sulphuric acid between 0·05 and 0·5 *N*. The maximum concentrations of sodium and potassium measured were 4 and 6 p.p.m., respectively, and at these levels no mutual interference was encountered in the sulphuric acid medium; the only direct interference encountered was from calcium, as noted by Jackson and Smith.[8] This effect was small, as both sulphate and aluminium ions depress the calcium emission, and could be ignored for calcium concentrations below 10 per cent. The use of an interference filter for sodium would reduce this interference to a still lower level.

DISCUSSION OF THE METHOD

ACCURACY—

Accuracy represents the degree of confidence that can be placed in a particular method of analysis and is determined by two factors, reproducibility (or precision) and bias. The former gives a measure of the random errors inherent in the method and the latter a measure of any systematic inaccuracies that can be eliminated by altering some aspect of the method.

Precision—A measure of the precision of the excitation and reading procedures is given in column 3 of Table III. These data were obtained from duplicate analyses on the same plate by using a single solution and can be used to assess the suitability of the chosen line pairs.

The precision of the complete method was determined from replicate analyses of one sample sparked in quadruplicate on six plates taken over a period of 6 weeks. The coefficient of variation for major constituents is not as low as that from standard chemical methods of analysis, but it is, however, of the same order as that found by other physical methods. The lack of precision is largely related to the use of much smaller sample weights and to errors that arise from plate-emulsion defects.

Bias—Bias is assessed by considering the difference between the observed, in this instance spectrochemical, and the "true" concentration, as determined by an independent chemical method, and should be considered in relation to the precision of either method

TABLE III

PRECISION OF THE PROPOSED METHODS

Compound determined	Amount of compound in the sample, %	Coefficient of variation for single determinations: Fusion method: Variations within the plate, %	Fusion method: Plate calibration data, %	Fusion method: Complete method, %	Wet-oxidation method, %
SiO_2	31·0	2·0	2·5	2·8	—
Al_2O_3	24·0	1·7	2·3	2·5	3·4
Fe_2O_3	6·55	1·9	2·0	2·2	2·5
CaO	11·80	1·9	1·8	2·4	3·3
MgO	2·45	1·7	1·9	2·4	3·3
TiO_2	0·77	2·3	2·5	2·8	3·1
Mn_2O_4	0·32	2·3	2·6	3·1	5·1
Na_2O	1·96	—	—	2·6	2·8
K_2O	0·62	—	—	2·4	2·1

before a decision is taken on its significance. The three most probable causes of bias associated with spectrochemical solution methods are (*a*) failure to obtain complete solution of the sample, (*b*) the use of unsuitable salts for calibration purposes, *e.g.*, hydrated salts that readily absorb moisture, or complex salts the composition of which may not be as specified, and (*c*) the possibility of inter-element effects.

Table IV gives a comparison between the results of the fusion and the classical methods of analysis for coal ash, flue dusts and slags of the type encountered in gas producers. Small deviations are apparent for calcium, magnesium and manganese. The lower chemical figures for calcium could arise from its incomplete precipitation as oxalate[9] and loss as sulphate on digestion of the sample. Any calcium not removed as oxalate would be determined along with magnesium to give high results for this element. This is confirmed by the results shown in Tables IV and V and is most apparent with large sample weights. A smaller sample was used for the analysis of the mineral matter in coal and these effects are therefore not evident in the results shown in Table VI. No comparison is available for copper, strontium and barium. The comparison with the colorimetric semi-micro method, shown in Table V, is equally as good as that with the classical method, and no bias for manganese is evident. The results of the chemical analyses for manganese are not of high accuracy and have not been subject to much consideration, as this element is of minor importance in the analysis of ash. The deviations for two samples were originally large and the chemical figures were subsequently amended, which indicates that the observed bias of −0·1 per cent. is probably of chemical origin.

The results given in Table VI verify the view that no loss of the major constituents occurs, within the limits of experimental error, when coal is ashed at 775° C. This has been confirmed by H. R. Brown, Officer-in-Charge, Coal Research Section, C.S.I.R.O., in a private communication. No chemical data for the alkalis were available, but the work of Logie and Raynor[10] indicates that no loss occurs on heating up to 1000° C.

CONCLUSIONS

Spectrochemical solution methods are readily applicable to the analysis of the mineral matter in coal, coal ash and a wide variety of associated minerals.

The mineral matter in coal itself can be analysed without prior ashing by using the wet-oxidation procedure to destroy the coal substance and to dissolve all the compounds except silica. These compounds, including the alkalis, are determined on one solution and silica is determined separately by a standard gravimetric procedure. Dissolution of ash is effected by means of an alkali-fusion technique, all compounds except the alkalis being determined in the solution of the melt. A second solution must be prepared by digestion with hydrofluoric acid for the determination of the alkalis.

The precision is of the same order as that for other physical methods, *i.e.*, ±2 to 3 per cent., and the proposed methods are some three or four times as rapid.

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Notes

THE DETERMINATION OF STARCH IN SAUSAGE MEAT AND CALCULATION OF THE NITROGEN CORRECTION FOR CEREAL CONTENT

THE method published by the Society for Analytical Chemistry for estimating meat content[1] relies on the Stubbs and More calculation, *i.e.*, an assessment of the amount of filler by means of a "difference" figure, followed by deduction of the filler nitrogen from the total nitrogen, after which the corrected nitrogen figure is related to lean meat by means of a factor. The method described for the determination of starch as a check on the amount of carbohydrate in the filler is rather cumbersome, and the proposed method for determining the cereal-nitrogen correction makes use of a procedure that has been applied to different types of wheat flour[2] and which is easier and more rapid.

Method

REAGENTS—

Acidified calcium chloride solution—Dissolve 620 g of calcium chloride hexahydrate crystals in 180 ml of distilled water and filter the solution until clear. Add a solution containing 18 g of sodium acetate trihydrate in 50 ml water to the clear filtrate and adjust the mixture to pH 2·3 by the addition of analytical-reagent grade glacial acetic acid. Adjust the specific gravity of the solution to 1·30 at 20° C.

Carrez's solution I—Dissolve 21·9 g of zinc acetate dihydrate and 3·0 ml of glacial acetic acid in 100 ml of water.

Carrez's solution II—Dissolve 10·6 g of potassium ferrocyanide in 100 ml of water.

PREPARATION OF THE SAMPLE—

Prepare the sample by passing it through a mincing machine and then mixing rapidly in a mortar.[1]

PROCEDURE—

Mix about 5 g of sample with 10 ml of water in a 400-ml tall beaker. Add 50 ml of acidified calcium chloride solution and heat in an autoclave for 10 minutes at a pressure of 15 lb. per sq. inch. Cool the mixture by immersion in cold water and transfer it to a 100-ml calibrated flask by washing with acidified calcium chloride solution until the volume is approximately 90 ml. Add 2·0 ml of Carrez's solution I, shake the mixture well and add 2·0 ml of Carrez's solution II. Shake the mixture again and then dilute to 100 ml at 20° C with acidified calcium chloride solution. Filter the dispersion on a Whatman No. 541 filter-paper. The filtrate should be perfectly clear. Discard the first 15 to 20 ml of filtrate and obtain the polarimeter reading at 20° C in a 20-cm tube on the subsequent runnings. If P is the reading at 20° C in a 20-cm tube and $[\alpha]_D^{20°}$ is 200, then the amount of starch present is given by—

$$\frac{P \times 10^4}{400 \times \text{weight taken}} \text{ per cent.}$$

If the reading is made with a saccharimeter and the reading is V, then the amount of starch present is given by—

$$\frac{V \times 0{\cdot}3462 \times 10^4}{400 \times \text{weight taken}} \text{ per cent.}$$

Determine the amount of nitrogen associated with this amount of starch in the filler by multiplying the starch content by 0·025. Carry out a Kjeldahl determination on the sample to find the total nitrogen content, correct the result for the filler nitrogen and relate the corrected figure to the lean meat content by means of the usual factors, *i.e.*, for beef, 100/3·4 and for pork, 100/3·6. If the total meat content is desired, carry out a fat determination.

Discussion

Three typical results on pork sausage are given in Table I. The results are slightly lower than those obtained by using the Stubbs and More calculation. This is probably because the Stubbs and More method assumes a rather lower nitrogen content in the estimated filler than would be usual in present-day sausage rusks.[3]

Table I

Determination of lean meat in pork sausages

Starch found, %	9·78	10·74	9·33
Nitrogen due to filler, %	0·24	0·27	0·23
Total nitrogen, %	1·59	1·45	1·67
Nitrogen due to lean meat, %	1·35	1·18	1·44
Lean meat found,* %	37·5	32·8	40·0
Lean meat found by Stubbs and More's method, %	38·3	33·6	40·6

* The factor used was 100/3·6.

If the proposed method were adopted for checking in manufacture, the true ratio of starch (determined polarimetrically) to nitrogen in the filler could be used instead.

The values suggested here are based on the figures found for the composition of many bulked samples representative of the types of flour available in the United Kingdom,[4] from which it can be seen that the mean starch to protein ratio is 7 to 1. Since flour protein is given by the percentage of nitrogen found multiplied by a factor of 5·7, the nitrogen correction corresponding to the amount of starch found is given by the percentage of starch found multiplied by a factor of 0·025.

Normally, a polarisation technique for the determination of starch in products such as sausage would be open to objection. Errors could be made due to (*a*) possible optically active constituents in the meat itself, (*b*) the degree of modification of the starch when the flour is made into rusks, and (*c*) the presence of other organic matter in the flour. The examination of both beef and pork by the proposed method has failed to show the presence of any optically active matter. Experiments on rusks by methods evolved for wheat flour[2] indicate that, on average, the modification of the starch during rusk manufacture necessitates only a small correction of its specific rotatory power from $[\alpha]_D^{20°} = 203$ to $[\alpha]_D^{20°} = 200$. The final objection, (*c*), has been dealt with by Clendenning[5] and for practical purposes is negligible.

The method is not intended to replace the other methods for determining meat content, but, because of its ease and speed of application, it could be used as a check on the Society for Analytical Chemistry's method and the Stubbs and More calculation, and would certainly provide a simple routine method. It would, of course, be unsuitable without modification if fillers such as soya or dried-milk powder were present.

We are indebted to Dr. S. M. Herschdoerfer for samples of rusks used in sausage making, and to the Government Chemist for permission to publish this Note.

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FLAME-PHOTOMETRIC DETERMINATION OF SILVER IN BLISTER COPPER

THIS investigation was undertaken in order to reduce the time taken in the routine assay of metallurgical products.

Rathje[1] has shown that silver can conveniently and accurately be determined by flame photometry; it was decided, therefore, to combine the precipitation of silver as halide[2] with the flame analysis.

METHOD

APPARATUS—

A Zeiss PMQ11 quartz spectrophotometer with flame attachment was used. The oxy-hydrogen flame, at pressures of 200 mm of hydrogen and 0·3 kg per sq. cm of oxygen, was found to be most satisfactory.

REAGENTS—

All reagents should be of recognised analytical grade.

Sodium chloride solution—A 20 per cent. aqueous solution.

Nitric acid, 20 per cent. v/v.

Nitric acid, 5 per cent. v/v—A 5 per cent. aqueous solution containing 1 per cent. of sodium chloride.

Nitric acid, diluted (1 + 1).

Nitric acid, concentrated.

Ammonia solution—Ammonia solution, sp.gr. 0·880, diluted (1 + 3) with water.

Silver nitrate.

Bromine.

PROCEDURE—

Weigh an amount of clean blister (2 assay tons*) to give a final solution containing about 50 p.p.m. of silver and dissolve it in sufficient concentrated nitric acid, about 225 ml, adding the acid in 30-ml portions. When the vigorous reaction has subsided, add 1 ml of bromine to oxidise the sulphur and set aside for 10 minutes. Add 50 ml of diluted nitric acid (1 + 1) and heat to dissolve any remaining copper. Boil the solution to remove bromine and nitrous fumes and then add 100 ml of water and 5 ml of sodium chloride solution. Boil the solution for a further 10 minutes and then set it aside in a dark place overnight.

Filter the cold solution through a Whatman No. 40 filter-paper and wash out the beaker thoroughly. Wash the filter-paper alternately with cold water and cold 5 per cent. nitric acid wash solution. When the copper has been removed, wash well with water. Place a clean 250-ml beaker under the funnel and pour 10 ml of ammonia solution over the precipitate and filter-paper. Allow to drain and pour a further 10 ml of ammonia solution through the filter-paper. Follow this with 20 ml of hot 20 per cent. nitric acid and then two further 10-ml portions of ammonia solution. Finally, wash the filter-paper three times with small portions of water. Make the filtrate up accurately to 100 ml with water and use this solution for the flame-photometric determination.

TABLE I

RECOVERY OF SILVER FROM BLISTER COPPER

The blister used in each test was known to give 25 p.p.m. of silver per assay ton in the final solution

Amount of sample taken, assay tons	Amount of silver added, p.p.m.	Amount of silver found, p.p.m.	Amount of added silver recovered, p.p.m.
2	Nil	51	1
2	10	59	9
2	50	101	51
1	50	75	50

Set the instrument to give full-scale deflection with a reference solution containing 100 p.p.m. of silver, 40 ml of ammonia solution and 20 ml of 20 per cent. nitric acid in a volume of 100 ml.

Prepare a calibration graph from readings taken on known concentrations of silver in ammonia solution.

* An assay ton is the weight of sample that must be taken so that 1 mg is equivalent to 1 oz Troy per ton, *i.e.*, in this work, 1 assay ton is 29·17 g, representing 1 ton of 2000 lb.

Results

The most suitable wavelength was found to be 338·3 mμ. The flame background at this wavelength was very small and, in practice, could be neglected. If accurate results are required, the background radiation can be measured at 335 and 341 mμ and allowed for in the usual way.

Results of some recovery experiments are given in Table I. The proposed method was compared with a method that involves cupellation and then weighing the silver bead produced. The results of three comparative analyses were as follows—

Weight of sample taken, assay tons	2	2	2
Silver found by proposed method, p.p.m.	48	53	49
Silver found by cupellation method, p.p.m. ..	46	54	48

The proposed method reduces working time to about 2 hours and obviates the necessity for cupellation. The calibration graph was found to be slightly curved and to approach a limiting value as the silver concentration increased.

No interference was noted from sodium or magnesium, as these were removed during filtration. None of the common metals interfered.

I thank the Roan Antelope Copper Mines Ltd. for permission to publish this Note.

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THE SIGNIFICANCE OF THE POINTAGE TITRATION IN THE CONTROL OF ZINC PHOSPHATING BATHS

The complete analysis of phosphating solutions can be carried out by such procedures as those of Bush, Higgs and Box.[1] However, in industrial operations, sufficient control is obtained by using the well known pointage titration. The pointage is usually defined as the titre of 0·1 *N* sodium hydroxide solution required to neutralise a 10-ml aliquot of the bath solution, phenolphthalein being used as indicator. The titration is variously stated to measure the total orthophosphoric acid[2] or simply the total acid,[3] as distinct from the free orthophosphoric acid, which is titrated when methyl orange is used as indicator. The reactions that occur and the way in which the total phosphate content can be related to the pointage are subjects seldom discussed.

Cupr and Hemala[4] studied the comparatively simple example of the titration of an acid solution of zinc orthophosphate with sodium hydroxide and considered that the precipitate was a mixture of zinc secondary and tertiary phosphates. Rathje[5] precipitated zinc phosphate by mixing solutions of a zinc salt, potassium dihydrogen phosphate and sodium hydroxide, and deduced that only in a certain range of concentrations is a precipitate of constant composition, $3Zn_3(PO_4)_2.Zn(OH_2)$, formed. In practice, complications arise owing to the fact that any heavy metals present in excess of the equivalent combined phosphate can also be expected to react during the pointage titration.

Experimental

Some data, which help to explain the reactions that occur, have been obtained during operation of a commercial nitrate-accelerated zinc phosphate bath at an operating strength of 70 to 80 points and a temperature of about 185° F.

Composition of precipitate—

The precipitate present at the end-point of the pointage titration was examined. The X-ray diffraction pattern was similar to that of hopeite, $Zn_3(PO_4)_2.4H_2O$. Analysis of ignited residues indicated the presence of 51·2 per cent. of zinc and 47·9 per cent. of phosphate, as PO_4. The formula $Zn_3(PO_4)_2$ requires 50·8 per cent. of zinc and 49·2 per cent. of phosphate. The results suggest that the precipitate is mainly zinc orthophosphate, $Zn_3(PO_4)_2.4H_2O$.

CALCULATION OF POINTAGE—

It was now possible to consider the separate contributions of free orthophosphoric acid and zinc dihydrogen orthophosphate in the bath to the titre at the phenolphthalein end-point. If these are termed titre 1 and titre 2, respectively, the following reactions can be postulated—

$$H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + 2H_2O \quad .. \quad .. \quad .. \quad .. \quad \text{titre 1}$$

$$3Zn(H_2PO_4)_2 + 8NaOH \longrightarrow Zn_3(PO_4)_2 + 4Na_2HPO_4 + 8H_2O \quad .. \quad \text{titre 2}$$

Pointage titres were calculated from these reactions for comparison with the observed values. The pointage was found after taking a 5-ml aliquot from a cooled sample and diluting it to about 50 ml with distilled water. Titre 1, the free orthophosphoric acid content, was determined by direct titration, methyl orange being used as indicator. Titre 2 was found after the total phosphate present had been determined by Gabrielson's ion-exchange technique,[6] in which the cooled solution is passed through a cation-exchange column. The results are shown in Table I, expressed as the amounts of 0·1 *N* sodium hydroxide solution equivalent to 10 ml of phosphate solution.

The results show that, although the pointage titration is a measure of the total phosphate content for the synthetic solution, it measures some constituent in addition to the phosphate content in the nitrate-accelerated bath. If alkali metals had been present equivalent to the nitrate content, the pointage titration would have been unaffected. It appeared, therefore, that heavy metals were present in excess of the zinc required for titre 2.

DETAILED STUDY OF SELECTED BATH—

The first bath in Table I was then studied in more detail. The major constituents, expressed in g per litre, were as follows: free acid, as H_3PO_4, 16·1; combined phosphate, as H_2PO_4, 19·5; nitrate, 51·2; zinc, 21·3; sodium, 7·1. Curves for potentiometric titrations with 0·1 *N* sodium hydroxide solution showed only one sharp inflexion at pH 4·28. After passage through a cation-exchange column, a further potentiometric titration curve showed points of inflexion at pH 4·65 and 9·06, which correspond to the first and second neutralisation stages of orthophosphoric acid.

TABLE I

CALCULATION OF POINTAGE

Free orthophosphoric acid (titre 1), ml	Zinc dihydrogen orthophosphate (titre 2), ml	Total acidity (titre 1 + titre 2), ml	Pointage found, ml
32·8	26·8	59·6	82·0
30·8	29·5	60·3	85·0
27·6	26·1	53·7	78·8
27·4	23·2	50·6	69·0
35·8	5·4*	41·2	41·3*

* Results from a synthetic solution prepared by dissolving zinc oxide in orthophosphoric acid.

A large excess of zinc is present over that equivalent to combined phosphate, so that to titres 1 and 2 there must be added a third titre, to account for this excess of zinc, which probably reacts in the following way—

$$3Zn^{2+} + 2Na_2HPO_4 + 2NaOH \longrightarrow Zn_3(PO_4)_2 + 6Na^+ + 2H_2O \quad .. \quad \text{titre 3}$$

Titre 3 was calculated from the analytical data and the calculated pointage (the sum of titres 1, 2 and 3) was compared with the observed value for the first bath in Table I. Titre 1 was 32·8 ml, titres 2 and 3 were 26·8 and 16·3 ml, respectively, thus giving a calculated pointage of 75·9 ml. The agreement between this figure and the observed pointage, 82·0 ml, is much better. The remaining discrepancy is probably accounted for by co-precipitation effects and the start of dissolution of the precipitate.

CONCLUSIONS

The results indicate, as one might expect, that the pointage titration for zinc phosphate baths (and probably also for iron and manganese phosphate baths) is a measure of the total orthophosphate, according to the usual definitions, only if other heavy-metal salts, such as zinc nitrate, are absent. In this instance, the combined phosphate (titre 2) can be approximately deduced from a separate free orthophosphoric acid titration. When zinc is present in excess of

combined phosphate, as in the commercial bath studied, such a simple calculation is impossible and the pointage titration is a measure of all the major active bath constituents, *i.e.*, free orthophosphoric acid, zinc dihydrogen orthophosphate and the accelerator.

I thank Dr. T. Emmerson, Director of Research, G.K.N. Group Research Laboratory, for permission to publish this Note and Mr. D. Wilkinson for carrying out the X-ray examination.

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A POTENTIAL SOURCE OF SAMPLING ERROR IN THE DETERMINATION OF NITROGEN IN TITANIUM ALLOYS

During the course of experimental work on the apparent segregation of nitrogen in large billets of titanium alloys, erratic results caused us to suspect that serious contamination by nitrogen could be caused during preparation of samples by milling or drilling in the manner customary for the sampling of metals. Solid specimens, millings and drillings taken at several cutting speeds, were prepared from two different types of titanium alloy to test the effects of drill speed, size and wear on contamination of titanium samples by atmospheric nitrogen caused by heating at the cutting edge of the tool. When drillings were compared with lump samples, the latter were pickled in dilute sulphuric acid (1 + 4) to remove worked layers and the small particles of cutting tool that were welded into the machined surfaces. Nitrogen was determined by a method used for steel, namely, Kjeldahl digestion with sulphuric acid and sodium sulphate and then steam-distillation from sodium hydroxide solution and titration of the ammoniacal distillate with 0·01 *N* hydrochloric acid. A solution of 3·5 g of the sample in hydrochloric acid was used for the determination.

The results on samples from an alloy containing 2·6 per cent. of chromium and 1·5 per cent. of iron are summarised in Table I. The results of experiments on drilling samples at several cutting speeds from an alloy containing 4 per cent. of manganese and 4 per cent. of aluminium are shown in Table II. Both alloys were fairly hard, their Brinell numbers being between 320 and 370.

Table I

Effect of the method of sample preparation on the apparent nitrogen content of a titanium alloy containing 2·6 per cent. of chromium and 1·5 per cent. of iron

	Method of sampling	Sampling tool	Speed of tool, r.p.m.	Cutting speed, feet per minute	Number of samples	Range of nitrogen results, %	Mean, %
Billet slice (11 inches × 11 inches)	Drilling	⅜ inch H	1000	98	10	0·046 to 0·058	0·0515
	Lumps	Hacksaw	—	—	12	0·038 to 0·040	0·039
Billet slice (9 inches × 9 inches)	Drilling	⅜ inch H	1000	98	4	0·053 to 0·058	0·0545
	Milling	1 inch MC	130	34	7	0·049 to 0·050	0·0495
	Lumps	Hacksaw	—	—	4	0·046 to 0·048	0·0465
Bar (¾ inch × ¾ inch)	Milling	1 inch MC	130	34	3	0·069 to 0·070	0·069
	Lumps	Hacksaw	—	—	5	0·037 to 0·039	0·0385

H = high-speed drill. MC = carbon-steel milling cutter.

With all drills it was found that with each successive hole drilled the apparent nitrogen content increased. Results seriously in error could be obtained before the drill became too blunt to use. The ⅜-inch carbide-tipped drill retained a sharp cutting edge for longer than a similar high-speed steel drill, but even the former was starting to show wear after drilling six holes each ½ inch deep.

TABLE II

EFFECT OF THE METHOD OF SAMPLE PREPARATION ON THE APPARENT NITROGEN CONTENT OF A TITANIUM ALLOY CONTAINING 4 PER CENT. OF MANGANESE AND 4 PER CENT. OF ALUMINIUM

Samples were taken from a billet 12 inches in diameter

Method of sampling	Sampling tool	Speed of tool, r.p.m.	Cutting speed, feet per minute	Number of samples	Range of nitrogen results, %	Mean, %
Drilling	¼ inch H	1000	98	13	0·035 to 0·097	0·0565
Drilling	¼ inch H or C	440	43	6	0·037 to 0·042	0·0385
Drilling	¼ inch H or C	150	14·7	6	0·035 to 0·038	0·037
Drilling	¼ inch H or C	80	7·9	6	0·035 to 0·037	0·0355
Drilling	1 inch D	25	6·5	2	0·037	0·037
Lumps	Hacksaw	—	—	12	0·030 to 0·038	0·034

H = high-speed steel drill. C = carbide-tipped drill. D = spearpoint carbon-steel drill.

The results show clearly that it is essential to drill at low speeds and with a relatively coarse feed, a freshly sharpened drill being used if contamination of the sample by nitrogen is to be avoided. Since this work was carried out, a general warning on errors in sampling titanium has been published,[1] and low cutting speeds with a feed rate of 0·005 to 0·006 inch per revolution have been recommended for drilling titanium alloys.[1,2] However, the magnitude of the possible error has not been generally known, and this Note is published to call it to the attention of chemists engaged in the analysis of titanium alloys.

We thank Mr. E. W. Colbeck, Metallurgical Director of Hadfields Limited, for permission to publish this Note.

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Received *May 7th*, 1957

A RAPID SPECTROSCOPIC METHOD FOR THE DETERMINATION OF WATER IN GLYCEROL

UNTIL recently, spectroscopic work in the infra-red region has been centred on the fundamental 2 to 15-μ region. The near infra-red region, 0·7 to 2·0 μ, is a region that is only recently beginning to be exploited. This region has a number of advantages over the fundamental region, *e.g.*, path lengths are measurable with a micrometer, and liquids can be contained in simple robust glass cells.[1]

A particular advantage of this region is that, when overlapping of absorption frequencies occurs in the fundamental region, a useful separation often exists between the combination frequencies. This occurs with the fully bonded hydroxyl-group bands of water and alcohols.[2] These bands are hardly separable at 3 μ, but the combination bands near 2 μ are clearly separated by over 300 cm^{-1}. This is the basis of the present method. A band at 1·93 μ, attributable to absorption due to water, is clearly separated from the band arising from the hydroxyl groups of the glycerol at 2·1 μ.

Typical spectra of two glycerols containing 1·82 and 9·85 per cent. of water are shown in Figs. 1 and 2. These spectra were measured with a Cary recording spectrophotometer, model 14, and a glass cell of path length 1 mm was used. The double-beam arrangement of the Cary instrument, with a glycerol containing a trace of water in the reference beam, was used to record difference spectra, which are also shown. Calibration of glycerols containing known amounts of water ranging from 1 to 20 per cent. with the optical density of the 1·9-μ band gave an excellent linear relationship.

The procedure for determining the water content of an unknown glycerol is merely to fill a 1-mm glass cell with the glycerol, scan the 1·9-μ region, determine the optical density of the 1·9-μ band and deduce the water content from the calibration curve. With the limited number of determinations so far made, the standard deviation corresponds to $\pm$0·06 per cent. of water over the range 1 to 20 per cent. on pure glycerols.

A number of typical results by this method on glycerols containing only water as impurity are shown in Table I and compared with results obtained by means of a Karl Fischer apparatus.

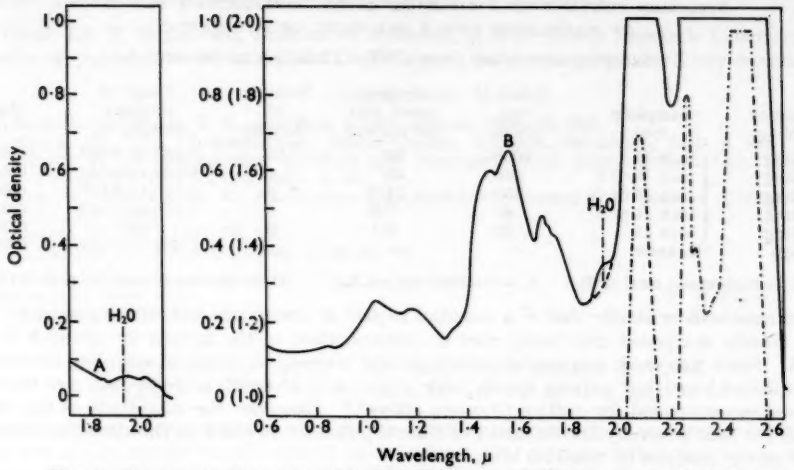

Fig. 1. Spectra of glycerol containing 1·82 per cent. of water: curve A, difference spectrum against water; curve B, near infra-red spectrum

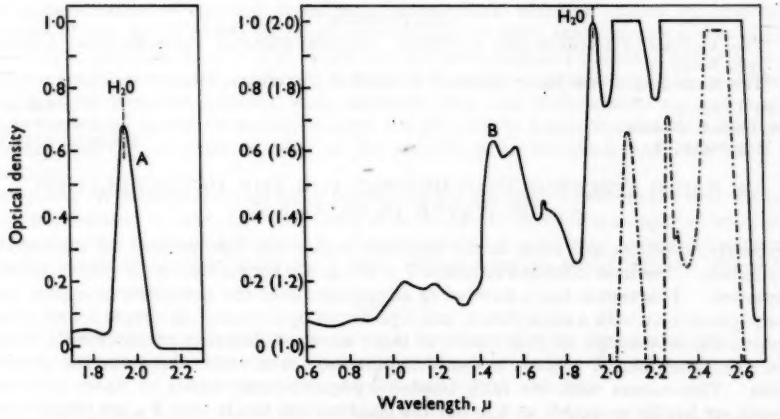

Fig. 2. Spectra of glycerol containing 9·85 per cent. of water: curve A, difference spectrum against water; curve B, near infra-red spectrum

TABLE I

COMPARISON OF RESULTS

	Water found by spectroscopic method, %	Water found by Karl Fischer method, %
Pure glycerol	0·45	0·42
	0·60	0·60
	0·84	0·78
	10·29	10·40
	19·1	19·41
Crude glycerol	6·89	6·82
	7·24	7·14
	7·63	7·55
	13·65	13·71

Some crude discoloured glycerols were also examined and their water contents determined by both methods; the results by the spectroscopic method were consistently higher (average error + 0·8 per cent.). This is considered to be due to scattered radiation from the dispersed salt and iron present in the samples. A constant correction factor improved the over-all agreement between the two methods.

A simpler instrument than the more versatile Cary spectrophotometer used in the present investigation could be devised to carry out this determination.

We thank T. H. Newlove and G. G. Jones for the moisture determinations with the Karl Fischer apparatus, and the Directors of Unilever Limited for permission to publish this Note.

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FINENESS OF FERTILISER SAMPLES

FOR a great many years we have found it possible to obtain concordant duplicates in fertiliser analyses by grinding to pass a 22-mesh sieve (British Standard 410:1943), which is a little finer than the sieve recommended in the 1955 Regulations, *i.e.*, "apertures about one-millimetre square."

Recently we have found that, with the more concentrated fertilisers, such as those having $N:P_2O_5:K_2O$ in the ratio of 10:10:16, it is impossible to weigh out duplicate 2-g portions that will give the same analysis. Inquiry showed that, for technical reasons connected with granulation, a new crystal form of ammonium sulphate is now favoured, namely, short thick prisms instead of needles. Examination with a low-power microscope indicates that this, together with the high proportion of ammonium sulphate, accounts for the separation and lack of uniformity (10 per cent. of nitrogen corresponds to about 47 per cent. of ammonium sulphate). We find that grinding to pass a 30-mesh sieve (British Standard 410:1943) makes it easy to obtain close duplicates, and microscopic examination of the more finely ground material shows that the crystals are largely fractured and that the tendency to separate is obviated.

It is hoped that the publication of this Note will save other analysts from some rather puzzling results.

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Received *December 19th*, 1957

A MICRODIFFUSION METHOD FOR THE DETERMINATION OF HYDROGEN SULPHIDE

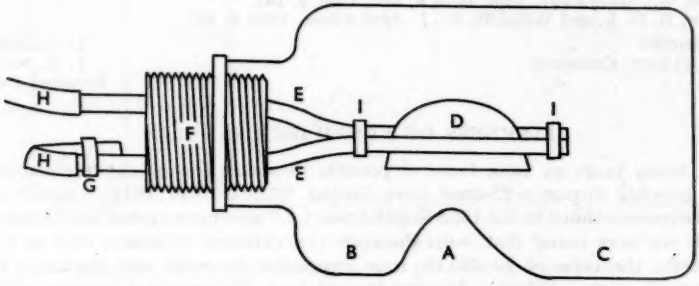
HYDROGEN sulphide either in biological materials or that liberated in enzymic reactions has frequently been determined by blowing the gas into a solution of a heavy-metal salt with a stream of nitrogen or carbon dioxide,[1,2,3] and then determining the heavy-metal sulphide either by titration[3] or colorimetrically.[1,2,3] Such methods suffer from the disadvantage that, when protein solutions are used, serious foaming is liable to occur.

The application of the well known principles of microdiffusion[4] to the determination of amounts of the order of 1 μg of hydrogen sulphide is described. The method is simple and the high sensitivity combined with the high rate of diffusion have permitted it to be used for more detailed studies of the kinetics of certain enzymic reactions in which hydrogen sulphide is liberated than could have been attempted by other methods. It seems possible that, with minor modifications, the method might be of fairly general use for determining small amounts of hydrogen sulphide.

A diffusion technique has been applied previously[5,6] to the determination of enzymically produced hydrogen sulphide, but the method was relatively insensitive and details of the rate of diffusion were not given. The method described by Conway on p. 244 of his book[4] also lacks high sensitivity.

In the proposed method, an apparatus (see Fig. 1) similar to that introduced by Brown *et al.*[7] for the determination of ammonia is used. A filter-paper, D, moistened with 0·01 ml of zinc acetate reagent solution (see p. 381) is held near the centre of a glass bottle of capacity about 50 ml, which

is rotated about its axis on horizontal rollers at about 120 r.p.m.; the hydrogen sulphide diffuses from the solution in the bottle on to the paper and is then eluted and determined colorimetrically. A groove, A, in one side of the bottle provides two separate compartments, B and C, when the bottle is held in the position shown in Fig. 1 and the solutions to be used are placed in these before the stopper and paper are inserted. Sometimes it is necessary to work under anaerobic conditions, and, when this is so, a stream of nitrogen saturated with water is passed through the assembled apparatus by way of the poly(vinyl chloride) and polythene tubes, H and E, for 5 minutes. The bottle is then closed by doubling back the poly(vinyl chloride) tubes, H, and securing them with the rubber bands, G (see lower tube H, Fig. 1); the nitrogen supply is then disconnected and the bottle is tilted to mix the contents of B and C and placed on the rollers for a suitable length of time.



A = Groove on one side of bottle
B = Upper compartment
C = Lower compartment
D = Filter-paper, diameter 2·3 cm, folded and held between polythene tubes
E = Polythene tubes, bore 1·5 mm
F = Soft rubber stopper
G and I = Rubber bands cut from rubber tubing
H = Poly(vinyl chloride) tubes

Fig. 1. Section through bottle

To measure the hydrogen sulphide taken up, the paper is removed with forceps and dropped into a test-tube containing 3·5 ml of amine reagent solution (see p. 381) and the tube is stoppered at once. The stopper is then removed momentarily, 0·5 ml of ammonium ferric sulphate reagent solution is added and the stopper is then replaced and the contents of the tube are mixed. The blue colour of the solution is measured with a spectrophotometer at 675 mμ, preferably 1 to 10 minutes after the addition of the oxidising agent, as slight fading sometimes takes place on standing.

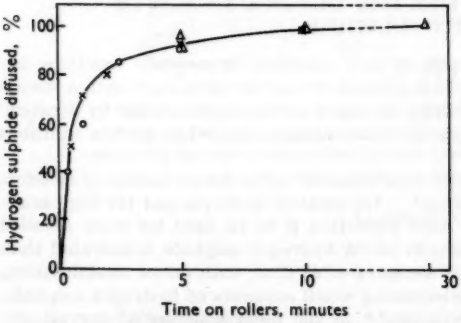


Fig. 2. Diffusion of 1·4 μg of hydrogen sulphide from phosphate buffer solution, pH 7, at about 24° C on to zinc acetate papers. Values are from several different experiments; the average recovery when diffusion was complete was 80 per cent. of that from experiments in which sodium sulphide solution had been added directly to the colorimetric reagents

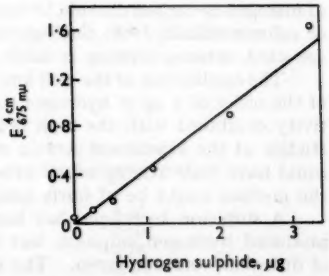


Fig. 3. Calibration curve for hydrogen sulphide prepared by diffusion from sodium sulphide solution and phosphate buffer solution for 8 minutes

Results with 2 ml of phosphate buffer solution at pH 7 in C and sodium sulphide solution in B are shown in Figs. 2 and 3. Fig. 2 shows that under the conditions used two-thirds of the hydrogen sulphide diffused in the first minute on the rollers and that diffusion was virtually complete after 5 to 10 minutes. Fig. 3 shows a typical calibration curve with different amounts of sodium sulphide solution and a rolling time of 8 minutes; the slight deviations from linearity shown appeared to be fairly reproducibile. In order to speed the diffusion in other work on total hydrogen sulphide determinations, it might well be advantageous to replace the phosphate buffer solution by a more acid medium; the pK value of hydrogen sulphide is about 7.

For determinations of enzymically produced hydrogen sulphide, the enzyme sample is placed in C and the substrate in B, and the tests are carried out in an atmosphere of nitrogen with the rollers inside a constant-temperature box. It may generally be assumed in such experiments, in view of the high diffusion rate shown in Fig. 2, that the rate of uptake of hydrogen sulphide by the paper is virtually equal to the rate of its production by the enzyme system; the method is therefore well suited for rapid studies of the kinetics of such enzymic reactions.

The reagents required are as follows (compare Johnson and Nishita[8])—

Zinc acetate reagent solution—A solution of 10 g of zinc acetate dihydrate and 2·5 g of sodium acetate trihydrate in 50 ml of water.

Amine reagent solution—A 0·01 per cent. solution of dimethyl-*p*-phenylenediamine sulphate (Hopkin & Williams Ltd.) in 1·5 per cent. v/v sulphuric acid. (This solution should not be stored for more than 1 week.)

Ammonium ferric sulphate reagent solution—A 2 per cent. solution of ammonium ferric sulphate in 1·5 per cent. v/v sulphuric acid.

I thank Professors F. Bergel and A. Haddow for their interest in this work, which was supported by grants from The British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund, the Anna Fuller Fund and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

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Book Reviews

Stability Constants of Metal-ion Complexes, with Solubility Products of Inorganic Substances. Compiled by Jannik Bjerrum, Gerold Schwarzenbach and Lars Gunnar Sillen under the Auspices of The International Union of Pure and Applied Chemistry. Part I: Organic Ligands. Compiled from publications earlier than January 1st, 1956, with collaboration by G. Anderegg and S. E. Rasmussen. Pp. xvi + 105. London: The Chemical Society, 1957. Price 60s. (Special Publication No. 6).

The ability to adjust the position of ionic equilibria in solution forms the basis of many analytical procedures. It is certainly true for qualitative and quantitative separations, for precipitation and solvent extraction, for masking and sequestration and in the production of coloured complexes for absorptiometry. But nowhere is the effect so apparent as in the use of aminopolycarboxylic acids (complexones), and Schwarzenbach has shown in his monograph on Complexometric Titrations (Methuen, 1957) how a knowledge of the relevant dissociation constants of proton - ligand and metal - ligand complexes permits a correct choice of conditions in, *e.g.*, the determination of hardness in water with EDTA and a metal indicator. Similar data are of great value for making an intelligent choice of masking agent and ascertaining the optimum pH for its use.

For some years a group of scientists has been collecting data on the stability of complexes and the present volume is a result of international co-operation directed by the Commission on Equilibrium Data of the I.U.P.A.C. The literature survey has been completed up to the end of 1955 and includes data for 464 organic ligands, which are listed in order of their empirical formula according to Beilstein's system. For each ligand, L, are quoted the stability constant for every published metal complex, the pK values for the conjugate acids HL, H_2L, etc., the methods used in their determination, the ionic strength and temperature of measurement and the literature references. To indicate the coverage, there are 11 stability constants itemised for the first entry (CH_2O_2, formic acid) and 30 for the last entry ($C_{32}H_{32}O_{12}N_2$, phthaleincomplexone), and no less than 148 under $C_{10}H_{16}O_8N_2$ (ethylenediaminetetra-acetic acid).

There are excellent indexes of metals and of ligands, a concise introduction that is an effective and brilliant survey of methods of measuring and computing stability constants and a most valuable 5 pages headed "How to use the tables." Publication by the Chemical Society as one of their Special Publications has enabled the price of this unique compilation to be kept reasonably low. Together with the companion volume dealing with Inorganic Ligands (which will shortly be published) this is certain to become an indispensable reference book for every up-to-date analyst.

H. IRVING

ORGANIC ELECTRODE PROCESSES. By MILTON J. ALLEN. Pp. xiv + 174. London: Chapman & Hall Ltd. 1958. Price 32s.

This book deals essentially with the instrumental methods that might be used by the investigator interested in the electrolysis of organic compounds and further with the products arising from their cathodic reduction or anodic oxidation. The publication gives useful information about the nature and yield of the products obtained in the electrolysis as well as the mechanism of the processes. Particular attention is paid to methods of electrolysis under controlled conditions. The literature has been covered very thoroughly, as is shown by the list of 464 references. At first sight it might be thought that this book will appeal mostly to organic chemists seeking new ideas on preparative methods; polarographers, however, interested in cathodic reduction and anodic oxidation processes, will find the publication worth studying. Moreover, one has the feeling after reading this work that analytical chemists have not paid as much attention to the electrolysis of organic compounds as they might profitably have done.

J. HASLAM

METHODS OF BIOCHEMICAL ANALYSIS. Volume V. Edited by DAVID GLICK. Pp. x + 502. New York and London: Interscience Publishers Inc. 1957. Price $9.50; 75s.

K. B. Augustinson of Stockholm contributes a chapter on assay methods for cholinesterases (ChE), which catalyse the hydrolysis of choline esters, acetylcholine being the most important. These enzymes are numerous and may also split non-choline esters and exhibit very different specificity patterns, but only those esterases that are inhibited by 10^{-5} M eserine should be designated ChE. Within the family of ChE enzymes there are two main groups—acetylcholinesterases (I) and a more heterogeneous group (II), including the unspecific ChE or pseudo ChE. The complicated problems that arise from this situation are surveyed clearly and in adequate detail.

An article on biological standards in biochemical analysis by J. H. Humphrey, D. A. Long and W. L. M. Perry emanates from the National Institute for Medical Research, London.

"Biological standards are necessary only for impure substances and their *raison d'etre* is evanescent, in that their useful life is limited to the time taken to elucidate, by biochemical analysis, their exact chemical composition and to prepare by synthetic methods their active constituents. Can the standards themselves aid in shortening this period, can they commit *felo de se*?"

With this as the main theme the authors say "drug control authorities speedily discovered that there was no way of eliminating animal variation and that the only way to reduce its effect on activity measurements was to carry out comparisons of the sample under test with a standard preparation, or reference substance, which was examined concurrently at every stage of the investigation."

After describing the arrangements for international co-operation, the authors proceed to discuss antibiotic standards, hormone standards, enzyme standards, miscellaneous pharmacological standards and finally immunological standards. It is interesting that the vitamin standards have served their turn and that, with the possible exception of cholecalciferol, they are not likely to be renewed when supplies are used up. This is an interesting and authoritative chapter.

The next chapter, by W. J. P. Neish of Sheffield (formerly of Edinburgh), surveys the different α-keto acids known to occur in plants and animals, and outlines the development of analytical methods. Preliminary chromatographic separations of α-keto acids can be carried out and the disadvantages of non-specific methods can thus be overcome.

Micro-methods for determining pyruvic and α-ketoglutaric acids are described, together with some apparently specific methods for determining these two acids and also oxalacetic acid, separately or in mixtures. This is a long and comprehensive article.

B. E. Saltzman and R. G. Keenan of the U.S. Public Health Service deal with the micro-determination of cobalt in biological materials, a problem of interest because of the role of cobalt in animal nutrition, in enzyme systems and in haemopoiesis *via* the cobalamines. Various colorimetric methods are described and a detailed procedure is given based on extraction with 1-nitroso-2-naphthol followed by spectrophotometric determination as the nitroso-R-salt complex (range 1 to 25 μg and sensitivity 0·1 μg). Emission-spectrographic techniques are also described.

New ground will be broken for many readers in the chapter by B. A. Loveridge and A. A. Smales of A.E.R.E., Harwell, on activation analysis and its application in biochemistry. "Many elements may be determined in the sub-microgram region by measuring the radioactivity induced when the sample is exposed to bombardment by nuclear particles. Neutrons are frequently used, but successful analyses have also been completed, using charged particles—protons, deuterons and helium nuclei—to create radioactive isotopes."

At first it was necessary to rely upon the particle-accelerating machines, but nowadays it is the "high neutron flux of the atomic reactor which has made radioactivation analysis a formidable tool for analytical purposes." The intensity of the characteristic radiation emitted after bombardment is linearly related to the weight of the stable isotope activated. A weighed sample and a reference standard (with a known proportion of the element under analysis) are subjected to nuclear bombardment side by side. A chemical separation is then needed to remove all other induced radioactivity and an inert carrier for the element under study may be used. It is quite clear that the method has very great possibilities; it is highly specific, reasonably accurate and reproducible, very sensitive, and, once the irradiation has been done, it is immune to contamination errors.

R. E. Thiers of Harvard contributes a chapter on contamination in trace-metal analysis and its control. He defines the "trace level" as 100 p.p.m. or less. "Contamination . . . is the presence of an error . . . due to the entrance (or exit) of unwanted, unexpected and usually unknown quantities of the substance being measured." This leads Thiers to the concepts of *positive* contamination, *negative* contamination and *pseudo*-contamination. To designate unduly low results due to unexpected losses as negative contamination is a somewhat curious use of words; in the main it refers in practice to losses incurred during dry-ashing. Incidentally, pre-ashing (with a hyphen) seems a little less disconcerting than *preashing*. This chapter must at one point or another be of interest to every analyst. It deals with handling samples, purifying reagents (including water), with the selection and cleaning of apparatus and with many ways of circumventing the consequences of contamination.

W. A. Bauld and R. M. Greenway of Montreal present an authoritative account of the chemical determination of oestrogens in human urine. The subject is discussed fully and the final procedures (*a*) based on adsorption chromatography of the methyl ethers and colorimetric determinations (J. B. Brown) and (*b*) based on column partition chromatography and colorimetric determination (Bauld) are set out in detail. Dr. Bauld devoted much time to this problem during his stay in Marrian's laboratory at Edinburgh and it is pleasant to read how successfully it has been solved.

H. Rosenkrantz of the Worcester Foundation, Mass., contributes a chapter on the infra-red analysis of vitamins, hormones and co-enzymes. He used throughout a spectrometer (Perkin-Elmer 12C) in which energy intensities between 3640 and 2500 cm^{-1} were sacrificed so as to obtain a relatively constant transmission line at lower frequencies. The samples were used as potassium bromide pressed prisms, a method of examination that eliminates solvents. More than half the absorption curves so obtained were checked against, and found to agree with, earlier records by other procedures for preparing the absorbing sample. The method of presenting curves is, unfortunately, on a scale that is linear neither to wavelength nor frequency. The commentary in the text is, however, very valuable in that special features of the spectra are noted; in any case many of the curves can, when necessary, be enlarged and studied carefully.

Rosenkrantz makes his point about the advantages of dispersing samples in potassium bromide, but does not overstate his case. In his conclusion he rightly says "interpretation of infra-red spectra comes with much experience and does not necessarily follow hard and fast rules."

Surveying this volume as a whole, it is impossible for anyone who has himself battled with troublesome analytical problems not to feel respect and admiration for the authors and for their work.

R. A. MORTON

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THEORETICAL CHEMISTRY: LOOKING BEFORE AND AFTER. By D. P. CRAIG. Pp. 14. London: H. K. Lewis & Co. Ltd. 1958. Price 2s. 6d.

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RECOMMENDED METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

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Errata

JANUARY (1958) ISSUE, p. 21, 2nd line, and p. 23, reference 7. *For* "Drysen" *read* "Dyrssen."

MAY (1958) ISSUE, p. 268, 10th name in Main Committee. *For* "N. T. Wilson" *read* "N. T. Wilkinson."